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A SOLVENT AND CATALYST-FREE APPROACH FOR SYNTHESIZING BIO-BASED ADHESIVE USING VARIOUS DIOLS

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A Thesis Submitted to the Graduate School
in Partial Fulfilment of the Requirements
For the Degree of
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Pittsburg, Kansas

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A SOLVENT AND CATALYST-FREE APPROACH FOR SYNTHESIZING BIO-BASED ADHESIVE USING VARIOUS DIOLS

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A SOLVENT AND CATALYST-FREE APPROACH FOR SYNTHESIZING BIO-BASED ADHESIVE USING VARIOUS DIOLS

An abstract of the thesis by
Sonu Parekh

The development of low-cost bio-based formaldehyde-free adhesives has aroused widespread interest in the adhesive industry. The usage of adhesives that contain urea-formaldehyde or phenol formaldehyde leads to environmental issues. Traditional polyurethane adhesives were based on fossil fuels and the use of solvents made them toxic. Petrochemicals are non-renewable resources that will be depleted soon. Therefore, non-renewable materials should be replaced by bio-based renewable resources. Using renewable bio-resources, especially plant oils, as a substitute for petroleum-based polyols is an approach that showed promise. Here, in this research work, soybean oil polyol (SOP) was used to synthesize polyurethane (PU) adhesive. For studying bonding strength, three different aliphatic diols: ethane-1,2-diol (EDO), 1,4-butanediol (BDO), and 1,6-hexanediol (HDO) with increasing chain length were used as a crosslinking reagent. For studying bonding strength, different wt.% of diols were used to synthesize PU adhesives. The bonding strength of these PU adhesives was observed on three different coupons (oak wood, maple wood, and stainless steel). Interestingly, on oak wood, the bonding strength was increased from 3 MPa to 6.36 MPa after incorporating 10 wt.% of BDO which is the highest bonding strength among all the other adhesive samples. In addition, on maple wood, the bonding strength was observed at 4.47 MPa to 7.79 MPa after adding 7.5 wt.% of HDO crosslinker in PU adhesive. Thermal properties of the synthesized adhesive were studied. A solubility test was also performed to check the solvent's effect on these PU adhesives and the degree of crosslinking. After being immersed in different solvents for 24 hours, there were no notable changes observed in the FT-IR spectra of these PU materials. Contact angle of these adhesives was above 90˚ confirming the hydrophobic nature. This work provides a sustainable alternative to petroleum-based adhesives with good bonding and physical properties without using solvents and catalysts.

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LIST OF ABBREVIATIONS

BDO	1,4 butanediol
CNT	Control
DSC	Different scanning calorimetry instrument
EDO	Ethane-1,2-diol
ESO	Epoxidized soybean oil
FTIR	Fourier transformed infrared
GPC	Gel permeation chromatography
HDO	1,6 hexanediol
PU	Polyurethanes
RT	Room temperature
SO	Soybean oil
SOP	Soybean oil polyol
TGA	Thermogravimetric analysis
WCA	Water contact angle

CHAPTER I

INTRODUCTION

Polyurethane (PU) adhesive plays an important role in daily life as these are polymeric materials that hold objects together. The primary function of a PU adhesive is to provide powerful bonds between different materials with higher bonding strength [1,2]. After modification of raw materials, it can be served in different forms for easy application on various surfaces like wood, metal, plastic, and fabric. A diverse class of adhesive formulations is commercially available with strong bonds, water resistance, and durability but petroleum-based adhesives are prepared using non-renewable materials, researchers are looking for alternative green materials and approaches to the synthesis of bio-based adhesives.

1.1 What is polyurethane?

The first PU was made by Otto Bayer and collaborators in 1937 through the reaction of diol and diisocyanate from a polycondensation reaction [3]. Industrial production of PUs began in 1952. The use of PU technology and the diversity of its applications benefits daily life. They can be synthetic or naturally occurring, serving numerous functions in many sectors. Polymers constitute large molecules made up of repeating smaller units called monomers [4]. PU are highly versatile polymeric materials with repeating urethane linkage [NH–C(O)–O]. The polymerization of the urethane linkage is mainly due to two functional groups, the hydroxyl (–OH) group and the second isocyanate group (–N=C=O) [5]. Polyester and polyether are common examples. Due to the urethane linkage, this reaction is known as polyurethane polymerization [6]. The formation of the urethane bond is shown in **Figure 1**.

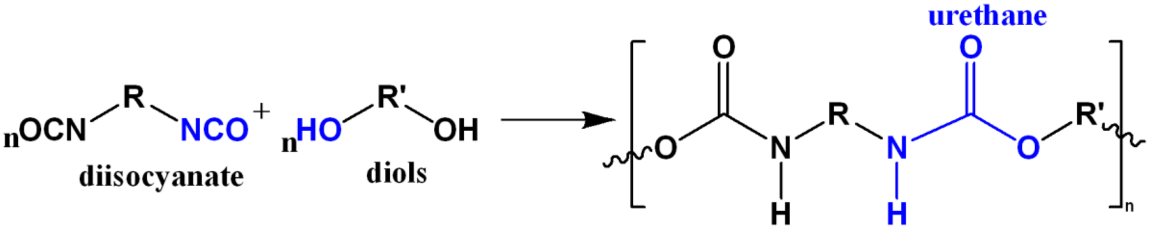

Figure 1: Reaction between isocyanate and polyol.

PU is most widely used in many applications, such as coatings, adhesives, sealants paints, flexible/rigid foams, and biomedical, automotive, and aerospace sectors [7]. Worldwide, PU was the sixth most produced polymer. In 2022 the global market with a value of $67.13 billion is estimated to reach $105.2 billion by 2025 [8].

Non-isocyanate polyurethane and isocyanate polyurethane are two separate classes of PU. Although non-isocyanate polyurethane was made through the reaction of cyclic carbonates with polyamines [9]. On the other hand, the isocyanate group participated in the formation of PU. In addition, the high reactivity of the isocyanate group (-NCO) is influenced by the positive charge on the carbon atom. In this functional group, carbon atoms have the lowest electron density while the oxygen atom has a higher electron density, and the nitrogen atom has an electron density with a negative charge (**Figure 2**). The intermediate negative charge acts as a nucleophile. The active proton of a hydrogen atom from the hydroxyl group has a nucleophilic center. Hence, the nucleophile (nitrogen) attacks the electrophilic carbon atom, which forms a new bond between the hydrogen and nitrogen atoms of the -NCO groups. This kind of reaction is related to the nucleophilic addition reaction, and results in the creation of a new chemical bond [10].

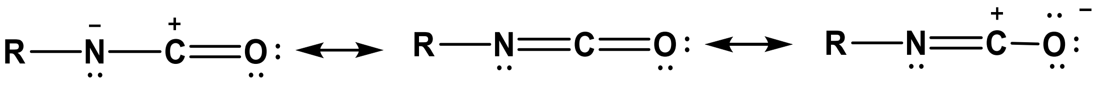

Figure 2: Representation of resonance structure of isocyanate.

Polyols play a crucial role in polyurethane because they have more than two hydroxyl groups [11]. In 2019, polyols had a market value of $26.2 billion, which is expected to reach $34.4 billion by 2024 [11]. The most utilized sectors are polyether, polyester, and acrylic polyols [12]. The properties of PU are significantly based on the functionality, structure, and molecular weight of the polyol used in the synthesis process. Different methods are used to synthesize the polyols for example, polyether polyols are made through the copolymerization of propylene oxide and ethylene oxide. Polyester polyols are synthesized through the reaction of diol (like ethylene glycol) with a dicarboxylic acid [12]. These two compounds, as well as their molar ratio, influence the properties of the polyester polyol [13]. Functionality is an important factor as high-functionality polyols (having more reactive groups) tend to form more cross-linked and rigid polyurethanes, while low-functionality polyols result in more flexible and elastic PU. Moreover, the molecular weight of the polyol influences the overall size and flexibility of the polyurethane chains. Low molecular weight polyols can form rigid and cross-linked structures; however, the higher molecular weight can give more elastic and flexible polyurethanes [14].

Traditional methods of synthesizing polyols are derived from fossil fuels and commercial ones. Nevertheless, due to growing environmental awareness, the emphasis on polyurethane research has pivoted towards vegetable oil and bio-based polyols [2,15]. To reduce the reliance on petroleum-based materials, researchers are exploring new ways for synthesizing bio-based polyols [3,15–17]. This includes green compounds derived from plants such as vegetable oils, and lignin. The object of this approach to PU production is to environmentally friendly and based on renewable resources. In this work, epoxidation and ring-opening reaction methods were used to convert soybean oil into polyol.

1.1.1 Types of polyurethane

PU is a polymeric material that is different in many ways compared to the other plastic types. PUs are used in many sectors like paints, coatings, elastomers, insulators, elastic fibers, etc. Mainly PUs are divided into five main types: rigid PU, flexible PU, thermoplastic PU (TPU), polyurethane ionomers (PUI), and waterborne PU (WBPU) [18,19]. Rigid PU foams are insulation materials, that are used in construction, refrigeration, and packing (**Figure 3**). Rigid PU provides thermal insulation and structural support [13]. Flexible PU foams are used in bedding, automotive interiors, and nanocomposites. TPU properties allow processing and recycling. The thermoplastic nature of TPU is due to the block copolymer structure, which provides hard and soft segments; hard segments are formed by the reaction between diisocyanate and low molecular weight chain extenders, providing rigidity and strength to the polymer. Soft segments are the result of diisocyanate and high-molecular-weight polyols and give flexibility, and elasticity to the material. TPU provides a variety of substrates that give good adhesion strength, for adhesives and coatings. It is useful in applications such as footwear, houses, and automotive parts [20]. PUI are polyurethane materials that incorporate ionic groups into the polymer structure. The ionic group can be used with specific monomers during the polymerization process, resulting in unique properties suitable for many applications like adhesives, sealants, medical applications (such as catheters and tubing), and automotive components [1,2,21]. WBPU is a polymeric material, which is dispersed in water instead of organic solvents. This environmentally friendly material has gained popularity. Applications of WBPU as coating and adhesives used in processes for bonding materials like paper or wood, in industries. It is also useful in construction, automotive interiors, and medical applications [22].

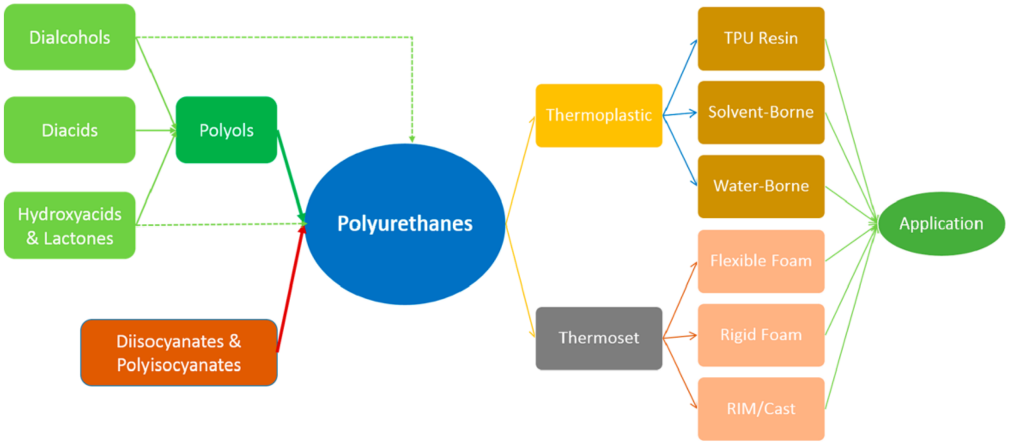

Figure 3: Types of polyurethanes. Reproduced with permission [22]. Copyright 2021, American chemical society.

1.1.2 Applications of polyurethanes

The demand for PU as an industrial polymer is increasing day by day due to its advantages like durability, having toughness of metals with the elasticity of rubber, and its chemical resistance. The global market for PUs was $67.13 billion in 2022. Increasing consumption of PUs-based materials would be continued growth at a rate of around 5.0 to 5.6% per year until 2025 [23]. This industrial demand comes from the diversity in applications for PUs, which include fibres, foams [24], elastomers [25], thermoplastics [26], adhesives [27], coatings [28], and sealants. PUs are also applied in biomedical applications, construction, automotive, textile, and other industries due to their properties including hardness, elongation, and strength [13].

PUs are extensively used in furniture manufacturing, particularly in the production of chairs, mattresses, and sofas. The flexible segment of PUs allows them to be soft and resistant to creep, which maintains the shape of the product. Memory foam is one of the examples, it adapts its shape according to the body to give comfort and is generally used in hospitals to relieve pressure sores [13].

The PUs are used for, automotive sectors including seats, armrests, and the interior sector. Their low weight is the key factor, but they also have strong mechanical properties, which makes them ideal for enhancing fuel efficiency and safety. To cite an example, PUs in seat cushions and padding due to their excellent cushioning properties, durability, and ability to be molded into different shapes. Additionally, PU foam is lightweight compared to traditional materials like cotton or rubber, which helps to improve fuel efficiency by decreasing the overall weight of the vehicle.

While, PU has low heat transfer properties making it an effective thermal insulator, which is applicable in the field of CO_2 emissions like refrigerators, and greenhouse gases. It contributes to energy savings by reducing the need for heating and air conditioning, which reduces hazardous gas [7].

PUs are stable against corrosion, heat, and radiation, making them suitable for bonding agents. They can be applied to various surfaces like rubber, wood, metal, and glass. Moreover, PU adhesive can be elastic or rigid, which depends on structure of material. In presence of moisture, the isocyanate is reacted with carbon dioxide and with humidity to form amine groups. Then, these amine groups react with isocyanate to produce a cured PU adhesive. Additionally, rigid PU can be cured by heat.

The chemistry behind the versatility of the urethane group is a major repeating monomer, made from the reaction between alcohol (-OH) and isocyanate (NCO), also containing other groups like ethers, esters, and urea which has a wide variety of sources can easily be synthesized for specific applications [16]. Hence, they have become one of the most active areas of polymers.

1.2 Role of isocyanate in PUs

The isocyanates, initially identified by Wurts in 1848, underwent comprehensive exploration throughout the nineteenth century by scientists such as Curtis and Hofmann [30]. Their application came in 1937 when Bayer and collaborators discovered polyurethanes [3]. Globally, isocyanates have become prominent in industry production. Isocyanate plays a crucial role in the formation of polyurethanes. In terms of polyurethane production, toluene diisocyanate (TDI) and methylene diphenyl isocyanate (MDI) are the most used chemicals. The mechanical properties of polyurethanes come from two physical-chemical processes between hard, and soft segments and hydrogen bonding between carbamate (or urethane) bonds. This reaction is known as polyaddition or polyurethane synthesis. Isocyanates react with the polyol in the step-growth polymerization process to form the urethane linkages (-NHCOO-). The main advantage of isocyanate chemistry is its high reactivity and the large yield of reaction as well as, low viscosity and low temperatures.

The isocyanate group is a linear structure, which has two cumulated double bonds (N=C) and (C=O) like other heterocumulenes. Based on the structure isocyanate is classified into two main categories: aliphatic and aromatic isocyanates. Aliphatic isocyanates are commonly known for UV stability and are less toxic compared to aromatic ones; hexamethylene diisocyanate (HDI) and isophone diisocyanate (IPDI) are examples. However, aromatic isocyanates have higher reactivity, higher bonding strength, and lower cost. Due to these advantages, aromatic isocyanates are widely used in synthesis. The reactivity of the isocyanate group is due to polarization induced by the high electronegativity of nitrogen and oxygen atoms. This reactivity can delocalize the electron density towards the nitrogen and oxygen atoms [31,32] In addition, isocyanates are commonly used as crosslinking agents in the production of coatings, adhesives, and sealants because they react with molecules containing active hydrogen, leading to the formation of a crosslinked structure. The highly reactive functional groups concerning isocyanate are alcohol, thiol, or amine. Isocyanates react with the hydroxyl group yields urethane; reaction with thiol yields thio-urethane; and reaction with amine yields urea bonds.

Isocyanates have valuable properties for various applications, but safety protocols are required for handling and storage because they can be toxic to the human body.

1.3 What is adhesive?

The adhesive is a material that is applied on two surfaces to join through an adhesive bonding process. The first literature on adhesives appeared in 2000 B.C. with simple procedures for making and using animal glue [33]. The first adhesive as a thermoset plastic, phenolic resin, was introduced in the market in 1920s [33]. Adhesives can bond wood to wood, and steel to steel, and used fibers to rubbers, etc. [34]. Adhesives exhibit favourable curing times, low temperature performance, pliability, high cohesive strength, and adhesion [35,36]. The adhesive is used in a wide variety of applications in different sectors such as packaging, furniture, aerospace, automotive, manufacturing, and woodworking industries. Adhesives can be made in two ways: petroleum-based and biobased. Petroleum-based adhesives are synthesized through the catalyst and solvent that have volatile organic compounds (VOCs) [37–39]. VOCs easily evaporate in the air and release harmful chemical gases that are toxic to both the environment and human health. To address this issue, scientists are moving forward in the development of biobased adhesive [40,41].

There are many different types of adhesives, such as epoxy-adhesive, thermoplastic, thermosets like acrylics, hot-melt adhesive, pressure-sensitive adhesive, water-based adhesive, UV/electron beam-curing adhesive, high-temperature adhesive [42]. Furthermore, their applications in different sectors include the automotive industry, where they are used in vehicle assembly for bonding components and reducing weight; construction for various applications like tiles, laminates, and insulation materials, woodworking for joining wood pieces in furniture; manufacturing, packaging; where they are used to seal boxes, attaching labels, bonding various packaging materials, electronics, medical industry, aerospace.

1.3.1 Adhesion

Adhesion is the interatomic and intermolecular interaction between two surfaces [43] such as a piece of wood and a second substance such as adhesive, coatings, or another piece of wood. This concept is different from cohesion which has only intermolecular forces inside one substance. Intermolecular forces exist in adhesion due to van der Waals forces [42]. There are many aspects important for wood adhesion such as mechanical interlocking, physical attraction, and chemical bonding of two surfaces [44]. Three factors are primarily important for adhesion. Physical bonding occurs due to van der Waals forces and electrostatic forces. Physical bonding is comparatively weak to chemical bonding because it contains the formation of atoms and molecules bonds. They are usually strong, but the strength of the bond is challenged by the interforce. Moreover, mechanical bonding of adhesion depends on the interlocking connection of components, the most prominent factor for strong joints [45]. Wood adhesion is quite difficult due to the physio-chemical characteristics of the wood source, and it depends on what type of wood is used for bonded assemblies.

Apart from that, other elements of joining surface like temperature, time, or load applied for cure also play a crucial role [46]. In addition, the material should be cured prior application of the adhesive. This is accomplished in many ways and involves polymerization. The mechanism of polymerization relies on a solvent, a catalyst, UV curing, crosslinker, and temperature.

1.3.2 Wood

Wood is a natural resource that is used as a substrate in many applications like furniture, paper, tools, buildings, flooring, particle board, and packing. Wood is a biopolymer component that has an interconnecting network of cellulose, hemicellulose, and lignin [47]. Cellulose is the basic structural component of wood, approximately 40-50% accounting in dry weight and long linear chains of glucose molecules give strength and rigidity to the wood fibbers. Wood cells have carbon (from 45 to 50% of the mass), oxygen (about 40−50%), hydrogen (about 6%), and nitrogen (less than 1%) [48]. There are two types of wood hard and soft wood. To cite an example, maple and oak are hardwood while pine and cedar are softwood.

In this work, oak wood and maple wood were used for bonding analysis because it has significant characteristics and applications. Maple and oak both wood are both hardwoods, but they have differences in terms of their chemical composition such as cellulose, lignin, tannin content, density hardness, and appearance. In terms of hardness, maple is slightly harder than oak. Both types of wood are used in furniture and heavy-use applications. The texture of maple wood is smooth rather than oak wood. From the previous research on oak wood, the cellulose, hemicellulose, and lignin proportions are (41%), (26.35%), and (25.71%), respectively [49].

Checking the bonding strength of the adhesive, a stainless-steel coupon was also introduced to study the bonding strength. Stainless steel is resistant to corrosion.

1.4 Petroleum-based wood adhesives

Most commercial adhesives are petroleum-derived, and their use is widespread in the adhesive market. Silicon-based adhesives (polydimethylsiloxane) have a significant output of more than $10.6 billion annually worldwide [50]. Formaldehyde-based adhesives are also used for many large-scale applications in industry due to their very highly reactive compound as well as chemical composition suitable for binders [51]. There are other fossil-derived polymers, such as polyurethane, urea-formaldehyde (UF), phenol resorcinol formaldehyde (PRF), phenol-formaldehyde (PF), melamine-formaldehyde (MF), melamine urea formaldehyde (MUF), and resorcinol formaldehyde (RF), epoxy-phenolics are the examples of thermosetting adhesives. A thermosetting synthetic resin is a linear macromolecule polymeric material that undergoes irreversible and physical changes during curing. Some thermosetting adhesives are based on condensation polymerization, which produces by-products and is followed by the addition of other polymeric materials for curing. They can provide high mechanical strength, good thermal stability, and low viscosity with great moisture resistance [52]. On the other hand, thermoplastic resin adhesives can be soft and melt when heated and become hard again when cooled. Chemical changes do not occur during this process and thermoplastic resins are recyclable adhesives [33]. Polyvinyl acetate and polyamide are two commonly used thermoplastic adhesives. Thermoplastic rubber is a new class of polymer adhesive, based on natural rubber or polybutadiene, which are block copolymers.

Hot-melt adhesives are sticky when heated and become a solid state when cooled, giving mechanical strength. The hot-melt method is used for fast production. Lower viscosity, a diluted polymer network, and enhanced heat resistance are important factors of hot-melt adhesive [53]. Additionally, adhesives for wood applications depend on other factors such as substrate surfaces, pH, presence of cross-linkers, binders, curing agents, solvents, catalysts, temperature, and UV radiation.

In addition, the use of solvent may emit VOCs during the application and curing, which helps to improve the strength of the polymeric material and increase the solubility; however, VOCs can contribute to indoor air pollution and have adverse health effects.

As a widely adopted technology, the predominant adhesive is coming from petroleum-based; however, environmental concerns are attached to their manufacturing and uses. The synthesis process releases hazardous gases that affect human health as well. Formaldehyde has a significant impact on wood adhesive because it provides higher mechanical strength, workability, quality, and economy but it is produced from non-renewable sources and releases low molar mass chemicals, which are harmful. This issue made their applications limited. consequently, scientists are moving forward to renewable sources to overcome cost issues and protect the environment.

1.5 Renewable source-based adhesive

In recent years, there has been a significant increase in the demand for “green” wood adhesives to improve the sustainability of processes and products. Thus, there is growing pressure on industries to adopt a more environmentally friendly synthesis path as well as to manufacture renewable products. Moreover, to reduce global pollution and mitigate climate change, authorities around the world have implemented strict rules and encouraged industries to heavily rely on biobased materials and processes. In addition, the future availability and cost of fossil fuels such as oil is also an important driver in moving forward to alternative sources of raw materials [54]. Furthermore, the adhesive industries have begun to avoid the use of solvents due to their significant impact on climate and human health. Hence, water-based adhesives are used as an alternative because of their lower VOC emissions and reduced toxicity.

Biobased adhesives are derived from organic, non-mineral sources such as lignin, tannin, protein, natural rubber, emulsion polymer carboxylic acid, and vegetable oil [55]. These materials include high hydrophobicity, low glass transition temperature (T_g), and low polydispersity. All properties that contribute to the effectiveness of adhesive [52]. Plant oils, such as soybean oil, castor oil, sunflower oil, palm oil, olive oil, linseed oil, canola oil, and castor oil [56–58] are inexpensive, sustainable, non-volatile, and naturally contain chemical functional groups like internal double bonds, or -OH groups, which can be modified and polymerized.

Making an adhesive requires modification of the polar groups that are present in the proteins and polysaccharides. Insufficient water resistance is often the major hurdle to be overcome. There are many ways to improve the water-resistance of adhesives based on biopolymers. For example, proteins can modify through tertiary and quaternary structures, which produce chemical crosslinking to create denser networks. This will allow the biopolymer adhesive to mix with synthetic adhesives. Moreover, renewable resources have been used to form macromolecules in polymer industries for the last decade. In this process, many diols such as 1,3-propanediol, and 1,4-butanediol participate in the polyester synthesis. Which comes from biorefineries. Other functional groups are glycerol and fatty acids [59]. which can be used directly or converted into new building blocks. Due to these opportunities, adhesives can be successfully synthesized from renewable sources; common examples are polyesters, polyurethanes, and epoxy-based polymers [54].

1.6 Soybean oil

The use of vegetable oils in polymer synthesis can contribute to the development of sustainable products and reduce dependence on fossil fuels, which saves the environment [60]. Some advantages of vegetable oils are biodegradability, low toxicity, sustainability, and industrial viability [61]. Vegetable oils including castor oil, sunflower oil, linseed oil, canola oil, soybean oil, etc are investigated as starting materials for polyols. In addition, these oils are also used as polymer additives like plasticizers to improve their flexibility and durability, and as a stabilizer to prevent or reduce the degradation of polymers due to heat, light, or oxygen. These oils can also be used as building blocks because their unique chemical structures allow them to be incorporated into polymer chains during synthesis, specifically in the case of thermoplastic polymers. Finally, they can be used as the raw material for the synthesis of cross-linked polymers that can irreversibly cure while encountering heat or other curing agents. The chemical composition of these oils allows for cross-linking reactions to occur, resulting in a more rigid and heat-resistant polymer structure [62].

Soy has been cultivated all around the world. The highest producers of soy are the United States, Brazil, China, and India. The United States is leading in the production of soy [63]. It would be cost-effective which can help to reduce the price of the desired material in this competitive era. Soybean oil is derived from the seeds of the soybean (Glycine max) and is characterized by its rich content of polyunsaturated fatty acids

(**Table 1**). This unsaturated oil can be modified for industrial use as biodiesel and utilized to make lubricants, plasticizers, etc. [61].

Table 1: Fatty acid content of Soybean oil

Unsaturated Fatty acid content	**Percentages (%)**
Palmitoleic acid	Traces
Oleic acid	22%
Linoleic acid	54%
Linolenic acid	7.5%
Arachidonic acid	Traces

1.7 Objective of this research

Formaldehyde and melamine-based wood adhesives are more popular for their good bonding strength and durability, but they are hazardous to climate and human health. Traditional methods for the synthesis of polyol were based on fossil fuels, these components are non-renewable and will be depleted soon. Hence, this research aims to find an alternative to petroleum-based wood adhesive without using solvents or catalysts. In this study, soybean oil is used as raw material to synthesize polyol for polyurethane adhesive. Soybean oil was converted into an isocyanate-reactive polyol through epoxidation and ring-opening reaction. The modification of polyol was confirmed by Fourier-transform infrared spectroscopy, hydroxyl value evaluation, and gel permeation chromatography. This research aimed to analyze the effect of crosslinkers such as ethene-1,2-diol, 1,4 butanediol, 1,6 hexanediol on the properties of PU adhesive. The bonding strength of adhesives was tested on oak wood, maple wood, and stainless-steel substrate. Apart from that, the impact on bonding strength was also carried out by using different curing temperatures and different weight percentages of diols. This research examined the physical properties, mechanical characteristics, and thermal stability of the adhesive made from soybean oil polyol.

CHAPTER II

MATERIALS AND METHODS

2.1 Materials

The materials employed in this study are represented in **Figures 4** to **8** with their chemical structure.

2.1.1 Soybean oil

Soybean oil was used as a starting material for the synthesis of bio-based PU wood adhesive. This process includes two steps: epoxidation of SO and the oxirane ring-opening of epoxidized SO. Soybean oil is a pale-yellow color oil obtained from seeds of glycine max [64]. It is composed of saturated, monosaturated, and polyunsaturated fats, which include five fatty acids: palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid. The percentage of these five fatty acids in soybean oil averages 10%, 4%, 18%, 55%, and 13%, respectively [65]. The double bonds present in the unsaturated fatty acid chains are transformed into vicinal hydroxyl groups. The soybean oil used in this experiment was purchased from a local Walmart (Pittsburg, KS, USA). **Figure 4** displays the chemical structure of soybean oil.

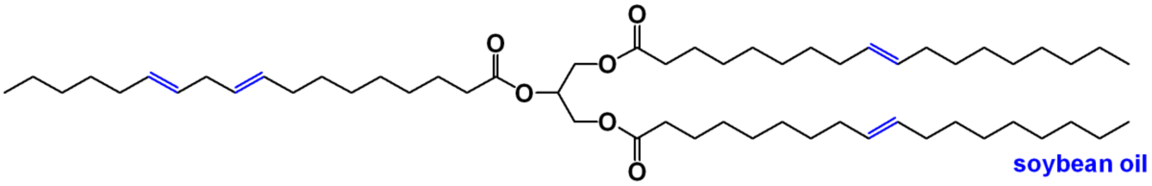

Figure 4: Chemical structure of soybean oil.

2.1.2 Isocyanates

Isocyanates are a functional group that reacts with hydroxyl groups. This functional group is primarily important for polyurethane synthesis. These are di-or polyfunctional (two or more than two -NCO groups per molecule), which can be aliphatic, aromatic, cyclo-aliphatic, or polycyclic in behaviour. For example, toluene diisocyanate (TDI), methylene diphenyl isocyanate (MDI), xylene diisocyanate (XDI), and meta-tetramethyl xylylene diisocyanate (TMXDI). The reactivity of isocyanates (R-N=C=O) depends on the aromatic or aliphatic group; Aromatic isocyanates are more reactive than aliphatic or cycloaliphatic isocyanates [64].

Two diisocyanates that are mostly used are TDI and methylene bis MDI and the higher oligomers for improved cross-linking. MDI is usually used for the formation of PUs comparatively to other isocyanates due to the lowest vapor pressure [66].

In this study, MDI was used for the formation of PU as an adhesive. MDI was gifted from Huntsman International LLC (The Woodlands, USA). The chemical structure of MDI is shown in **Figure 5**.

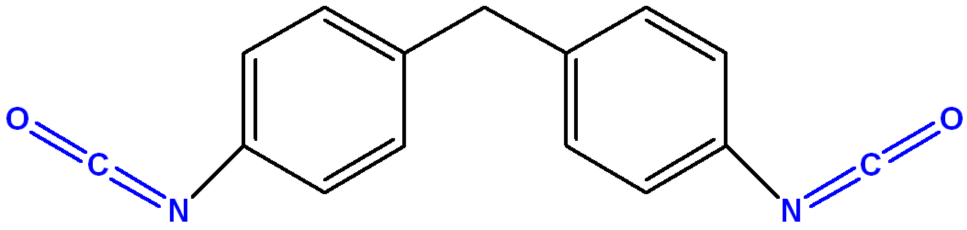

Figure 5: Chemical structure of MDI.

2.1.3 Chain extender

Different types of crosslinkers, fillers, and chain extenders are used in polymer to enhance their thermal and mechanical characteristics. Getting good bonding strength in control samples, three different diols with various carbon chain lengths were introduced namely, ethane-1,2-diol (EDO), 1,4-butanediol (BDO), and 1,6-hexanediol (HDO). These three were introduced as a chain extender to improve the bonding strength of polyurethane adhesive [67].

2.1.3.1 Ethane-1,2-diol

Ethane-1,2-diol is a versatile chemical with various industrial applications, which has two carbon atoms, six hydrogen atoms, and two oxygen atoms. **Figure 6** shows the chemical structure of EDO. This material was purchased by Fisher Scientific (New Jersey, USA). For the better bonding mechanisms of adhesive intermolecular hydrogen bond interaction is a prominent factor. In addition, the curing of adhesive is dependent on functional groups, and they relate to each other and become crosslinking structures that give good mechanical properties [68]. Here, diols were used to improve the characteristics of the PU adhesive adding more hydroxyl groups to crosslink with MDI.

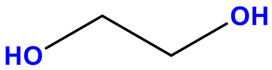

Figure 6: Chemical structure of ethane-1,2-diol.

2.1.3.2 1,4-Butanediol

1,4-Butanediol was introduced to increase the adhesive's performance. It contains two hydroxyl groups, which attach the first and fourth carbon atoms of a four-carbon chain. BDO was purchased from Fisher Scientific (New Jersey, USA). The chemical structure is shown in **Figure 7**.

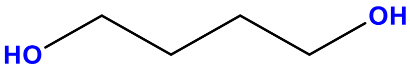

Figure 7: Chemical structure of 1,4-butanediol.

2.1.3.3 1,6-Hexanediol

1,6-Hexanediol was used as the third diol in this study. HDO has six carbon atoms with two hydroxyl groups attached at positions 1 and 6. It was purchased by Fisher Scientific (New Jersey, USA). The chemical structure is shown in **Figure 8**.

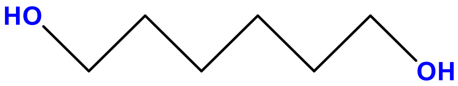

Figure 8: Chemical structure of 1,6-hexanediol.

2.2 Synthesis of polyol from soybean oil

To make the bio-based polyol from soybean oil, an epoxidation reaction and ring-opening reaction were used. The chemicals used in the preparation of polyol such as glacial acetic acid, Amberlite ion exchange resin, toluene, hydrogen peroxide, Lewatit MP64 resin, sodium chloride, sodium sulfate, tetrafluoro boric acid (TEBA), and methanol were bought from Fisher Scientific in Allentown, PA, USA.

2.2.1 Epoxidation of soybean oil

Epoxidation is a chemical reaction that introduces an epoxide group (known as an oxirane group) into a molecule. An epoxide group consists of a three-membered ring containing an oxygen atom. The synthesis route of epoxies from alkenes (C=C) can be made through four different methods: Conventional chemical treatment, Acid ion exchange resin, Enzymatic methods, and Metal catalyst method [69]. Nevertheless, the reaction of alkenes with peracetic acid (peroxyacetic Acid) offers several advantages such as simplicity of reagents, mild reaction conditions, and the ability to control the degree of epoxidation by arranging the stoichiometry of the reagents. This reaction is used on an industrial scale due to its high conversion rate and viability.

In this process, acetic acid serves as an oxygen donor, while hydrogen peroxide behaves as an oxygen transporter. When these two compounds react, peracetic acid is produced. Further, peracetic acid plays a crucial role in breaking the double bonds present in the oil, as a result epoxide ring is formed (**Figure 9**). The effectiveness of this reaction depends on factors such as temperature, catalysts, and environmental conditions [70].

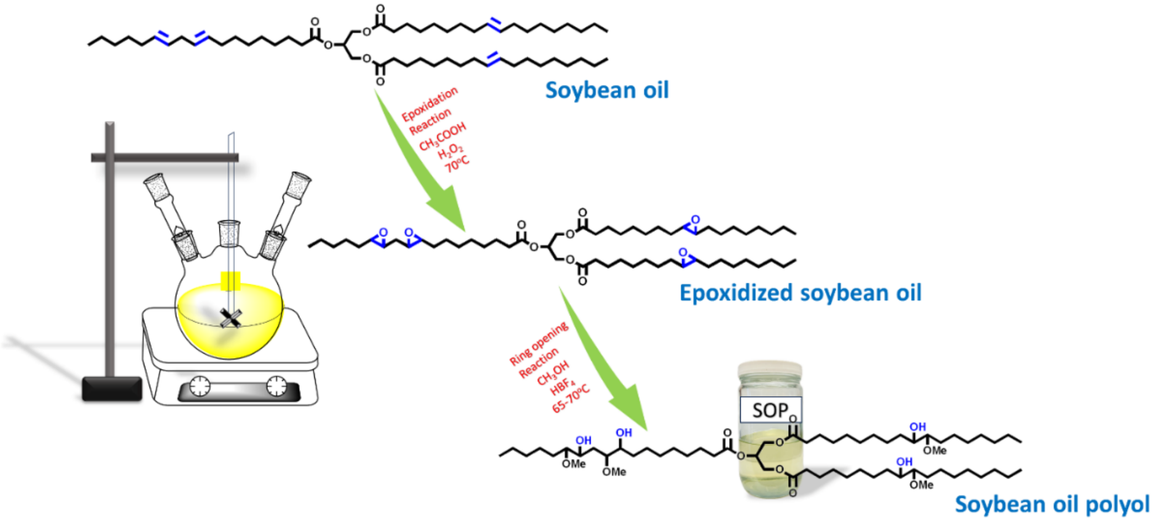

Figure 9: Reaction scheme for the synthesis of soybean oil-based polyol.

The epoxidation process was executed for the conversion of double bonds into the epoxy groups. Initially, 500 g of SBO and 250 mL of toluene (50 wt.% of SBO) were mixed in a three-necked round-bottom flask. Then, 125 g of Amberlite IR 120H resin (catalyst) was added. The mixture was mixed for 15 minutes to observe homogeneity. Afterward, 78 mL of acetic acid was gradually added drop by drop over 30 minutes using a dropping funnel. Here, the dropwise addition is important for safety reasons to escape possible superheating. The mixture was further stirred for 30 minutes to stabilize the temperature. Furthermore, in the same way, 442 mL of a 30 wt.% hydrogen peroxide (H_2O_2) solution was added to the mixture while keeping the temperature between 5 °C and 10 °C. Then after, the temperature was increased, maintained at 70 °C, and stirred for 5 to 7 hours following the complete addition of H_2O_2 in the same condition. Due to the chemical reaction between acetic acid and H_2O_2, peracetic acid was formed which can further react with a double bond situated in the chemical structure of SBO. When the reaction was completed, the mixture exhibited a color transition from orange to yellowish. In the next step, the mixture was cooled down at room temperature and then filtered to extract resin. The mixture was then washed 7 to 8 times with 10% brine solution until the pH was obtained 7 and, then anhydrous sodium sulfate (Na_2SO_4) was added to remove moisture and then separated with the funnel, remaining solvents were displaced from the mixture via rotary evaporation for 3 hours. Obtained ESBO was examined using confirmatory tests such as FT-IR, epoxy number, and GPC.

2.2.2 Ring-opening of ESBO into polyol

Typically, the basic structure of an epoxy ring includes oxygen connected to two neighboring carbon atoms. This arrangement creates an electrophilic site within the ring. The nucleophilic attack occurs when a molecule has a hydroxyl group and approaches the strained epoxy ring [70]. This leads to the opening of the ring. In addition, mainly alcohols (both mono-alcohols and diols) and carboxylic acids are used for ring-opening reactions because they react relatively quickly and efficiently. Nevertheless, weaker nucleophiles such as amines, water, and thiols have been investigated and demonstrated slower reaction rates. This means that they can participate in the ring-opening reaction, but the process is much slower than the strong nucleophiles [71,72].

In this work, this process was performed to introduce the hydroxyl functional group into the final product (polyol), The molar ratio for methanol and epoxidized oil was 7:1. In the initial step of the reaction, tetrafluoro boric acid at a concentration of 0.05% of the total weight of the mixture was chosen as a catalyst. The desired amounts of methanol and HBF_4 were added to a three-necked round-bottomed flask, and mechanically stirred, at 65-70 °C. Epoxidized oil was added dropwise, and the reaction was allowed to stir continuously for 90 minutes after the complete addition of epoxidized oil. The mixture was then cooled down at room temperature after Lewatit MP64 resin was added to the mixture. This mixture was again stirred for approximately 45 minutes and then filtered to remove the moisture and resin after performing the pH test to confirm the neutral mixture. Finally, rotary evaporation was done to remove the excess methanol present in the mixture. The obtained polyol was characterized. The illustration of the ring opening and epoxidation of soybean oil is presented in **Figure 9**.

2.2.3. Preparation of adhesive

Solvent and catalyst-free adhesives were prepared at room temperature by adding polyol and isocyanate with diols of different chain lengths. First, polyol and diols (EDO, BDO, HDO) were mixed in a glass vile. In the next step, MDI was added and then the mixture was stirred with a glass rod until it became homogeneous (**Figure 10**). For synthesizing PU-adhesive materials, different weight % of diols with different chain lengths were used. The adhesive samples containing EDO were cured at 75 ℃ and BDO and HDO were cured at room temperature (RT). The details of the amount of polyol, diisocyanate, and chain extenders are provided in **Tables 2,3** and **4**. To analyze bonding strength, oak wood, maple wood, and stainless-steel specimens were selected. All samples were prepared in the same way and three specimens were made for each sample to get the average bonding strength of the adhesive. By executing this process, the control sample for the PU adhesive was acquired.

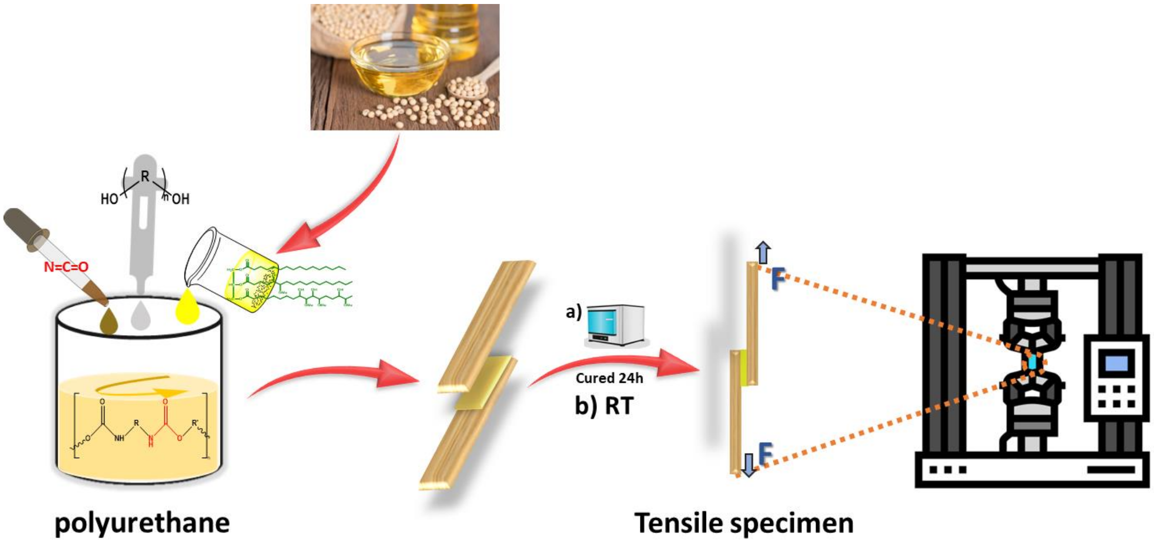

Figure 10: Schematic of preparation for adhesive

Figure 11 depicts the interaction of MDI, diol, and polyol. Here, the crosslink structure can be formed by the reaction of the isocyanate group of MDI with the hydroxyl groups of diols and polyols. Polyol exhibits a soft segment, while diol undergoes an isocyanate reaction to form a hard segment [22].

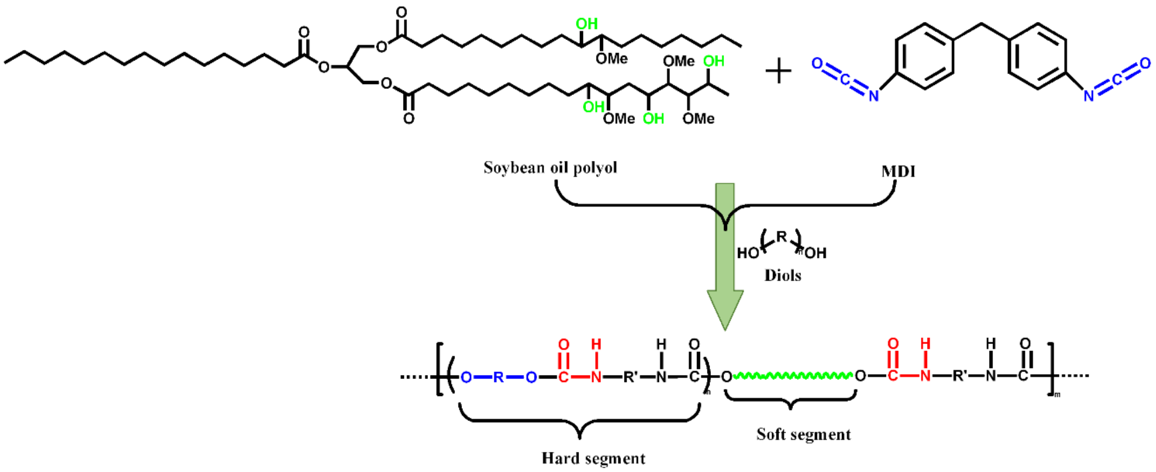

Figure 11: Reaction scheme of PU adhesive.

Table 2: Formulation table of the adhesive sample with EDO.

Sample code	SOP (in gram)	MDI (in gram)	Wt.%	EDO (in gram)
EDO -CNT	1	0.43	0	0
EDO -2.5	1	0.54	2.5	0.025
EDO -5.0	1	0.65	5	0.050
EDO -7.5	1	0.76	7.5	0.075
EDO -10.0	1	0.87	10	0.100
EDO -12.5	1	0.98	12.5	0.125
EDO -15	1	1.01	15	0.15

Table 3: Formulation table of the adhesive sample with BDO.

Sample code	SOP (in gram)	MDI (in gram)	Wt.%	BDO (in gram)
BDO -CNT	1	0.43	0	0
BDO -2.5	1	0.50	2.5	0.025
BDO -5.0	1	0.58	5	0.050
BDO -7.5	1	0.65	7.5	0.075
BDO -10.0	1	0.73	10	0.100
BDO -12.5	1	0.81	12.5	0.125
BDO -15	1	0.89	15	0.15

Table 4: Formulation table of the adhesive sample with HDO.

Sample code	**SOP (in gram)**	**MDI (in gram)**	**Wt.%**	**HDO (in gram)**
HDO -CNT	1	0.43	0	0
HDO -2.5	1	0.49	2.5	0.025
HDO -5.0	1	0.54	5	0.050
HDO -7.5	1	0.60	7.5	0.075
HDO -10.0	1	0.66	10	0.100
HDO -12.5	1	0.72	12.5	0.125
HDO -15	1	0.78	15	0.15

The adhesive mixture was used within 2 min of its preparation and was applied to two pieces of dried maple and oak wood samples **Figure 10**. Both the pieces were overlapped to 25 mm × 25 mm (length × width) areas, clamped manually, and cured for 24 h at different temperatures such as RT, 45°C, and 75°C. Among all temperatures, the most effective curing condition for enhancing the mechanical strength of PU adhesive was observed at 75°C and room temperature. These results will be elaborated further. All samples of adhesives were produced using the same methodology.

2.3 Characterization of soybean oil-based polyol

2.3.1 Iodine value

The iodine value is used to determine the degree of unsaturation present in a fat or oil. Unsaturated fatty acids contain double bonds, and the iodine value indicates how many grams of iodine can be reacted by 100 g of fat or oil [70]. Here, the number of double bonds in soybean oil was confirmed by the Hanus titration method.

2.3.2 Epoxide number

The epoxide number indicates the number of epoxide groups (oxirane rings) per unit mass or unit of a certain functional group in a molecule. Glacial acetic acid and tetraethylammonium bromide were used. To perform this test, 0.2 g of epoxidized soybean oil was dissolved in 50 mL of tetraethylammonium bromide (TEAB) solution. For titration, 0.1 N perchloric acid was taken and titration was performed after adding a drop of crystal violet as an indicator to the solution. The titration was completed when the color changed from blue to green, and the measured volume helped to determine the amount of epoxy present in the epoxidized soybean oil. This test was repeated 2 more times and the average value of a total of 3 tests was taken for confirmation then further reaction of soybean polyol was performed.

2.3.3 Hydroxyl value

The hydroxyl number is a measure of the amount of hydroxyl (OH) group in a chemical compound. It is an important parameter to confirm the -OH value of polyol, which provides information about the functionality and the required amount of isocyanates for an effective chemical reaction. In this work, ASTM-D 4274, (the phthalic anhydride pyridine (PAP)) technique was used. First, in a glass bottle, 10 mL of hydroxyl solution was mixed with 0.6 g of soybean polyol. The bottles were loosely capped and placed in a preheated oven at 100°C for 70 minutes. During that time, the solution was shaken every 15 minutes. The mixture was then settled down at room temperature, and 10 mL of HPLC-grade water and 20 mL of isopropanol were added. This mixture was mixed for 10 min. Lastly, the titration was done by the addition of 1 N NaOH until a pink color appeared. The amount was calculated and the hydroxyl number.

2.3.4 Acid value

The acid value, as determined using the IUPAC 2.202 standard procedure, around 1 g of the sample was dissolved in 30 mL of the solvent mixture (isopropanol, toluene, and phenolphthalein indicator). Then after 0.1 N potassium hydroxide was added gradually until a pink color shift was observed. The measurements were used to calculate the acid value. For the soybean polyol formulation 0.37 mg KOH/g. this means that 0.37 mg of potassium hydroxide (KOH) was required to neutralize the acidic components present in one gram of soybean polyol.

2.3.5 Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FT-IR) is an analytical technique for identifying the existence of functional groups, and chemical bonds. At room temperature, it shows spectra between 4000 cm^{-1} and 500 cm^{-1}. Spectra are recorded depending on transmittance (%) and wavenumber (cm^{-1}). The PerkinElmer Spectrum Two FTIR Spectrophotometer (**Figure 12**) was used to analyze the spectral data of starting material and synthesized materials.

Figure 10: Fourier-transform infrared spectroscopy.

2.3.6 Viscosity

Viscosity is the measurement of the resistance of the flow of a substance. Viscosity is directly proportional to molecular weight. If molecular weight is high viscosity should be high. An AR 2000 dynamic stress rheometer (TA instruments, USA) as shown in **Figure 13** was used for this testing. The viscosity was measured at 25°C with shear stress increasing from 1 to 2000 Pa linearly. The dynamic rheometer was equipped with a cone plate having an angle of 2° and a cone diameter of 25 mm.

Figure 11: AI 2000 dynamic stress rheometer for measuring viscosity.

2.3.7 Gel permeation chromatography

Gel permeation chromatography (GPC) is used to segregate the material’s size based on its molecular weight. GPC is also known as size exclusion chromatography. The significant impact of GPC is to analyze the retention time of the material which helps to confirm the successful conversion of the synthesized material. Additionally, retention time is directly correlated to molecular weight as the higher the retention time, the lower the molecular weight of the material. In this work, the Waters GPC instrument used was from Milford, MA, USA (**Figure 14**). THF was used as the solvent with a flow rate of 1 mL/min at 30°C.

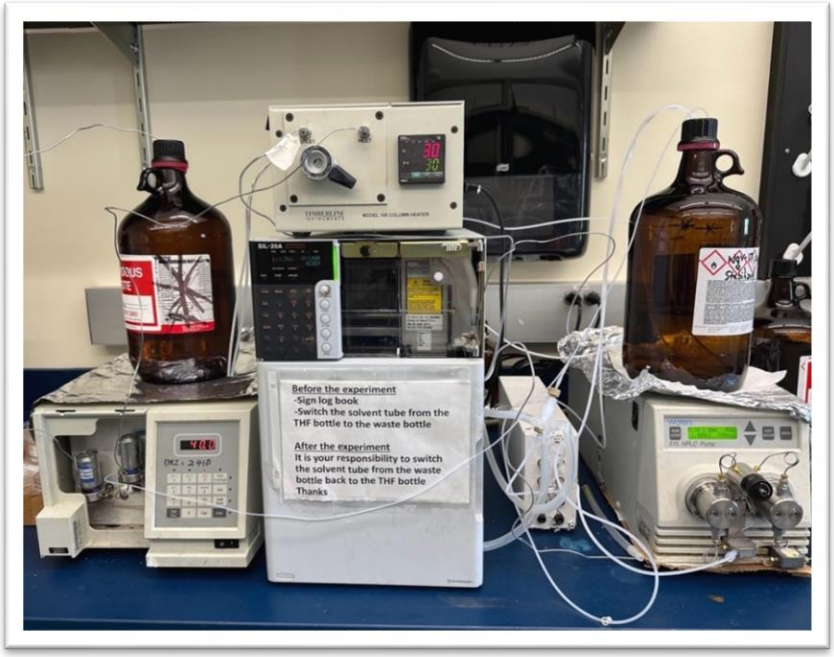

Figure 12: Gel permeation chromatograph.

2.4 Characterization of adhesives

2.4.1 Thermogravimetric analysis

The TGA (Q500, Discovery, Trios, USA) instrument as shown in (**Figure 15**) was used to study the thermal properties of the material. 10 mg of the specimen was loaded in the platinum pan. The samples were heated from 25 to 600°C under nitrogen with 100 mL /min purging flow at constant heating rates of 10°C /min. The thermal stability of the adhesive was ananalyzedhrough the TGA instrument.

Figure 13: Thermogravimetric analysis.

2.4.2 Different scanning calorimetry

Here, a different scanning calorimeter instrument was used for the thermal analysis of samples. This test measures glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature I. All DSC tests were performed using DSC Q100 (TA Instruments, USA) as shown in **Figure 16**. Testing of adhesive samples typically involved 5-15 mg of samples within an aluminum pan. This test carried out under a nitrogen gas purge flow of 40 ml/min with the temperature range was set to -50 to 300 °C with a 10°C /min ramp rate.

Figure 14: Differential scanning calorimetry instrument.

2.4.3 Bonding strength measurement

The ASTM Standard Procedure D2339-98 was used to measure the bonding strength of the material bonding strength measurement was conducted using the Instron model 3367 (Instron, USA) as shown in **Figure 17** with a 10 mm/min crosshead speed. Oak and maple wood and stainless-steel samples with an application area of 25 mm × 25 mm (length × width) were used to perform tests. The bonding strength under maximum load is the average obtained from measurements made on three separate specimens.

Figure 15: Bonding strength measurement instrument.

2.4.4 Contact angle

This instrument was used to study the hydrophobic nature of the materials. Which, contact angle (WCA) measurements were performed using Ossila Contact Angle Goniometer as shown in **Figure 18**. To perform this test, three different solvents were used, a droplet of 10 μL of solvent was dropped on the surface of the samples at room temperature, to study the hydrophobicity of adhesive samples.

Figure 16: Ossila water contact angle instrument.

2.4.5 Degree of swelling and gel content

The degree of swelling gives information regarding a polymer's capability to absorb and retain a solvent; however, the gel content is the insoluble fraction of a cross-linked polymer. In addition, the degree of swelling test involves immersing a cured adhesive sample in a solvent for a specific period. After the immersion, the swollen samples are weighed, and the degree of swelling is calculated as the percentage inclined in weight compared to the initial dry weight of the sample.

The gel content test assesses the extent of cross-linking in a cured adhesive. This test was performed with a cured adhesive sample when samples were dissolved in a solvent to extract the soluble components. The remaining insoluble gel fraction is then dried in an oven for 48 hours and weighed. The percentage of gel content was calculated with the original weight of the sample and dried weight after extraction.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of soybean oil-based epoxy and polyol

Characterization of the synthesized ESO and polyol was accomplished using the International Organization for Standardization (ISO) and American Society for Testing and Materials (ASTM) procedures, and all the characteristic data are presented in **Table 5**.

Table 5: Characterization table of SOP.

Parameter	**Unit**	**Soybean oil**	**Soybean oil Epoxidized**	**Soybean oil polyol**
Iodine value	g 1_2/100 g	132.27	1.84	-
Epoxy value	%	-	7.41	0.22
Hydroxyl number	mg KOH/g	-	-	180.89
Acid value	mg KOH/g	0.17	1.29	1.10
Viscosity@ 25°C	Pa. s	0.023	0.172	2.38

3.1.1 Iodine value

The iodine value of the SO and any unreacted double bonds on the SOP were calculated using the Hanus technique based on IUPAC 2.205. The iodine value is used to calculate the value of unsaturation or the number of double bonds in soybean oil and its polyol. The iodine value of soybean oil and polyol was observed to be 132.27, and 1.84 g/ 100 g, respectively.

3.1.2 Hydroxyl number

The hydroxyl number was evaluated using the phthalic anhydride pyridine (PAP) method based on IUPAC 2.241. Measurement of -OH number in polyol is essential because this function group is important for PU reaction. The -OH value of SOP was observed to be 180.89 mg KOH/g.

3.1.3 Epoxide value

Using glacial acetic acid and tetraethylammonium bromide, the proportion of oxirane oxygen on the ECO was determined. After the epoxidation reaction of soybean oil, the epoxide number was measured and found to be 7.41%, and this value declined in SOP to 0.22%. These results show that the epoxy group was successfully converted into the hydroxyl group.

3.1.4 Viscosity measurements

Viscosity is a measurement that indicates the material’s flow. Here, SBO, ESBO, and SOP’s viscosity were measured to be 0.02, 0.17, and 2.37 Pas. The viscosity was increased from SO to SOP due to the intermolecular interactions. The van der Waals weak interactions in soybean oil made it easier to flow. After the epoxidation and ring-opening reaction viscosity was increased due to the -H bonding.

3.1.5 Fourier-transform infrared spectroscopy

FTIR spectra determine the characteristics functional groups present in SO, ESO, and SOP. The stretching vibration of C=C and alkene C-H (=C-H) of SO was confirmed by the peaks that appeared at 1650 cm^{-1} and 3007 cm^{-1} respectively [72]. These two peaks disappeared, in the FTIR spectra of epoxidized soybean oil, and a new distinctive peak was observed at 840 cm^{-1} attributed to C-O-C in the epoxy oxirane groups. This outcome attests to the success of our epoxidation reaction method, even with highly viscous oils. After the ring-opening reaction, in the IR spectra of SOP a new peak was noted at 3365 cm$^{-1,}$ which confirms the presence of hydroxyl group (-OH). This observation indicates the ring-opening of the epoxidized oil, leading to the formation of -OH groups (**Figure 19**) [73].

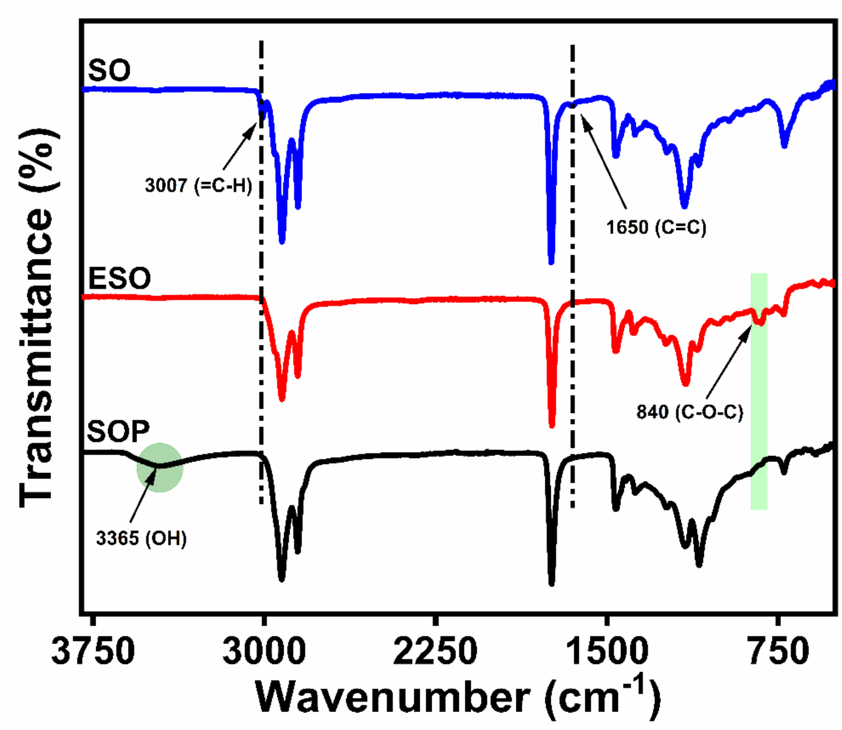

Figure 17: FT-IR spectra of SO, ESO and SOP

3.1.6 Gel permeation chromatography

After the successful modification of soybean oil into the ESO and SOP, the samples were tested by GPC to observe the reaction progress. Polymeric beads that make up the stationary phase have small pores so that larger molecules can pass through without being trapped. Changes in retention time can be seen in **Figure 20**. The retention time of SO, ESO, and SOP was 32.01, 32.24, and 31.99, respectively. The higher hydrogen bonding in SOP likely explains why its retention time was shorter than ESO and SO. The viscosity and molecular weight of SOP are raised because of stronger intermolecular forces caused by increased -H bonding [73]. Dimers, which are by-products of the ESO to SOP conversion, are likely responsible for the appearance of a shoulder peak at a retention duration of around 30.40 minutes. It is crucial to closely observe the reaction process to comprehend the development of both the targeted product and any by-products.

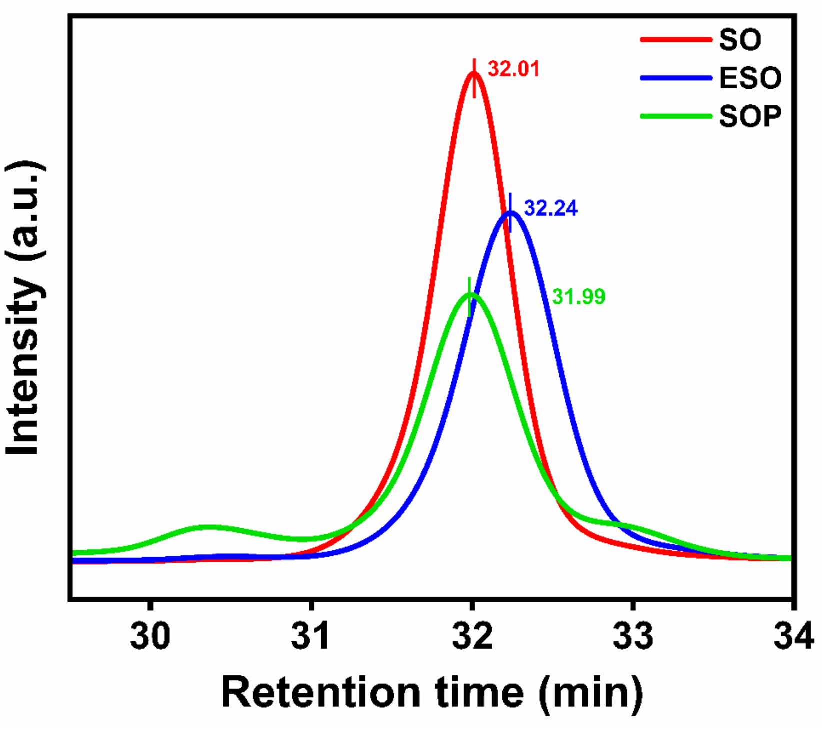

Figure 18: GPC results for soybean oil (SO), epoxide soybean oil (ESO), and soybean oil polyol (SOP)

3.2 FT-IR of PU adhesives

The FT-IR spectra of prepared adhesive and monomers are displayed in (**Figure-21 a, b** and **c**). In starting materials (EDO, BDO, HDO, and SOP), the hydroxyl group was found at around 3300 cm^{-1} [74,75]. -CH stretching vibration was observed at around 2872 cm^{-1} and 2940 cm^{-1} [76]. The peak for isocyanate (N=C=O) was found at 2255 cm^{-1} in pure MDI [77]. This peak totally missing from the adhesive samples with EDO. However, BDO and HDO containing adhesive samples exhibit unreactive isocyanate peak. The isocyanate peak weakens and vanishes in BDO and HDO as the aliphatic diol concentration in SOP rises (**Figure-21 d, e,** and **f**), showing that isocyanate group has successfully completed its reaction [78–80]. The hydroxyl group vanished, and the new peak arose in the adhesive sample which confirms the presence of the -NH group at 3300 cm^{-1}, -CO-NH group at 1718 cm^{-1}, aliphatic N-H stretching at 1518 cm^{-1} and C-N stretch at 1204 cm^{-1} confirms the formation of urethane linkage in adhesive materials [81].

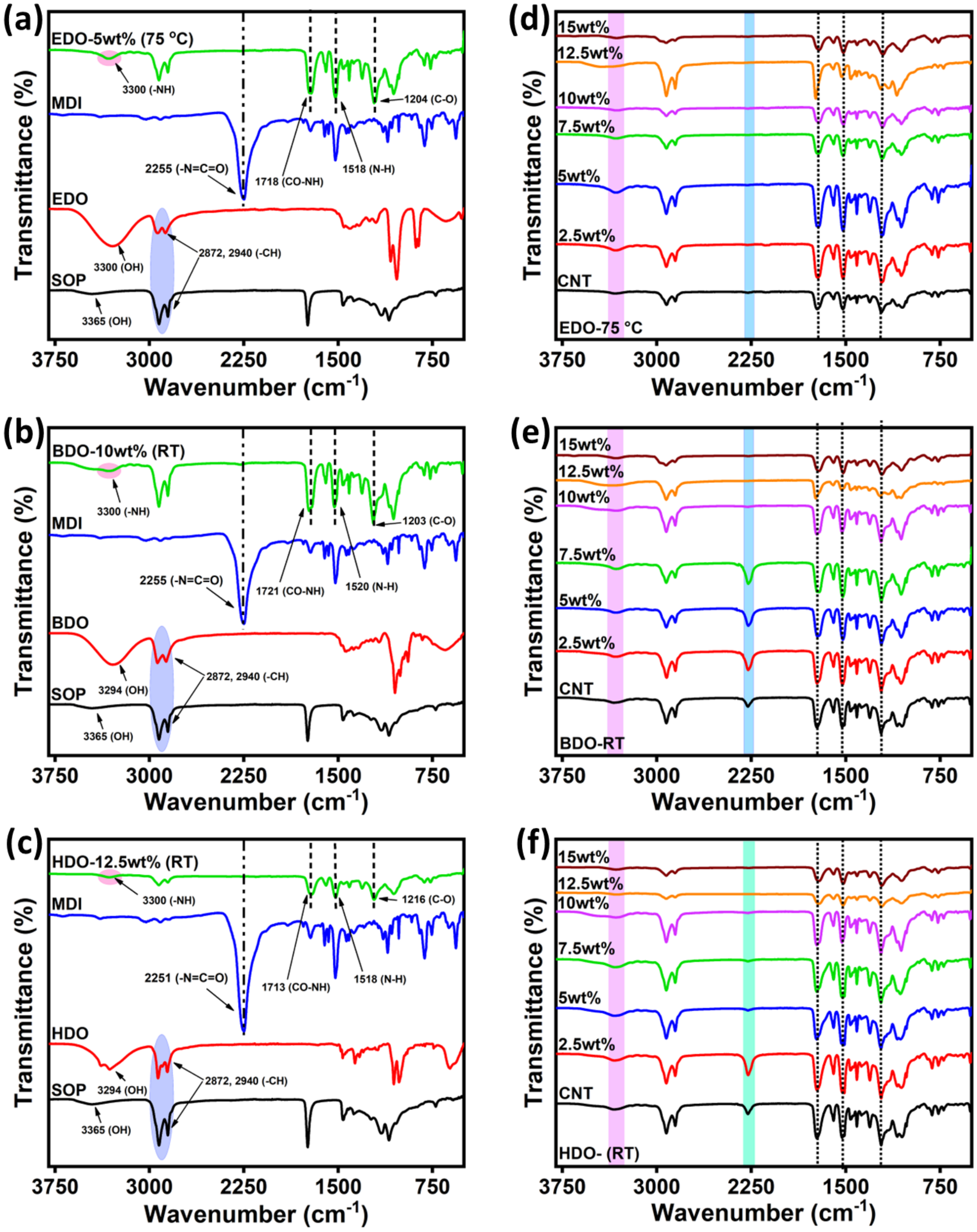

Figure 19: FT-IR spectra of (a), (b) & (c) comparison of EDO, BDO, and HDO wt.%, respectively with monomers, (d), I & (f) varying wt.% of EDO, BDO, and HDO, respectively in PU adhesive samples.

3.3 Bonding strength

3.3.1 Bonding strength on oak wood

Figure 22 shows the bonding strength of adhesives on oak wood. The bonding properties of the adhesive were found to be changed as the amounts of crosslinkers varied. For the curing of all samples, two different temperatures were used: 75℃ for EDO and was at room temperature for the BDO and HDO samples. These two temperatures were decided by performing trial testing of bonding strength with different temperatures to evaluate which temperature was appropriate for curing and higher bonding strength (**Figure 22**). After getting good results of bonding strength further testing was continued according to the best temperature for each crosslinker. Moreover, the adhesive was mixed with various weight percentages of EDO, BDO, and HDO. The bonding strength of the control sample was 2.39 Mpa at 75℃ and 3.23 Mpa at room temperature without any chain extender. There is an increasing trend in bonding strength up to 5 wt.% in EDO, 10 wt.% in BDO, and 12.5 wt.% in HDO. For the samples made with EDO crosslinker, it was cured at 75℃, the bonding strength was 3.43 Mpa with 2.5 wt.% increased at 4.25 Mpa for 5 wt.%, after that the downward trend was observed from 3.88 Mpa to 3.23 Mpa with increased wt.%. While BDO and HDO-based samples were cured at room temperature. Furthermore, BDO was incorporated, and the bonding strength went up from 4.21 Mpa (2.5 wt.%) to 6.36 Mpa (10 wt.%) and then the trend decreased to 4.12 Mpa with 15 wt.%. Additionally, the adhesive sample with HDO crosslinker shows enhancement in bonding strength from 4.78 Mpa to 5.5 Mpa till 12.5 wt.% then bonding strength was dropped to 5.21 Mpa with 15 wt.%. However, in the adhesive sample, each sample behaves differently. Interestingly, higher incorporation of a chain extender led to a more rigid and brittle structure, reducing the material's ability to absorb stress, and resulting in lower bonding strength, this may be a reason behind the decreasing trend in bonding strength [82]. BDO-based adhesive shows higher bonding strength compared to HDO and EDO because HDO contains six carbon chain lengths, due to the long chain length it may have slower reactivity compared to BDO and EDO. While BDO could fast react with isocyanate which can lead to more crosslinking within the adhesive matrix, resulting in higher bond strength. However, EDO has a short chain length, it contains only two carbons. Hence, steric hindrance may be the reason for lower adhesion strength comparatively BDO. With less steric hindrance, EDO molecules can't easily access and react with isocyanate groups. To analyze the higher crosslinking degree of BDO-based adhesive, a solubility test was performed and BDO shows the higher gel content, which clearly defines that higher crosslinking imparts greater bonding strength and rigidity to the material, making it more resistant to deformation. Also, the bonding strength on stainless steel metal coupons is tested using the best adhesive sample of each crosslinker. The bar graph (**Figure 23d**) illustrates that EDO-5 wt.%, BDO-10 wt.%, and HDO-12.5 wt.% had 1.31Mpa, 3.79Mpa and 2.83Mpa respectively. Hence, on the metal coupons BDO shows higher bonding strength rather than EDO and HDO. The equation utilized for the determination of the bonding strength is as follows: F_{max} represents the maximum force applied (N), a indicates the surface area of the adherend (mm^2) while a and b respectively refer to the width and length of the adherend (mm).

$$\text{Bonding strength (Mpa)} = F_{max} / A = F_{max} / a \times b$$

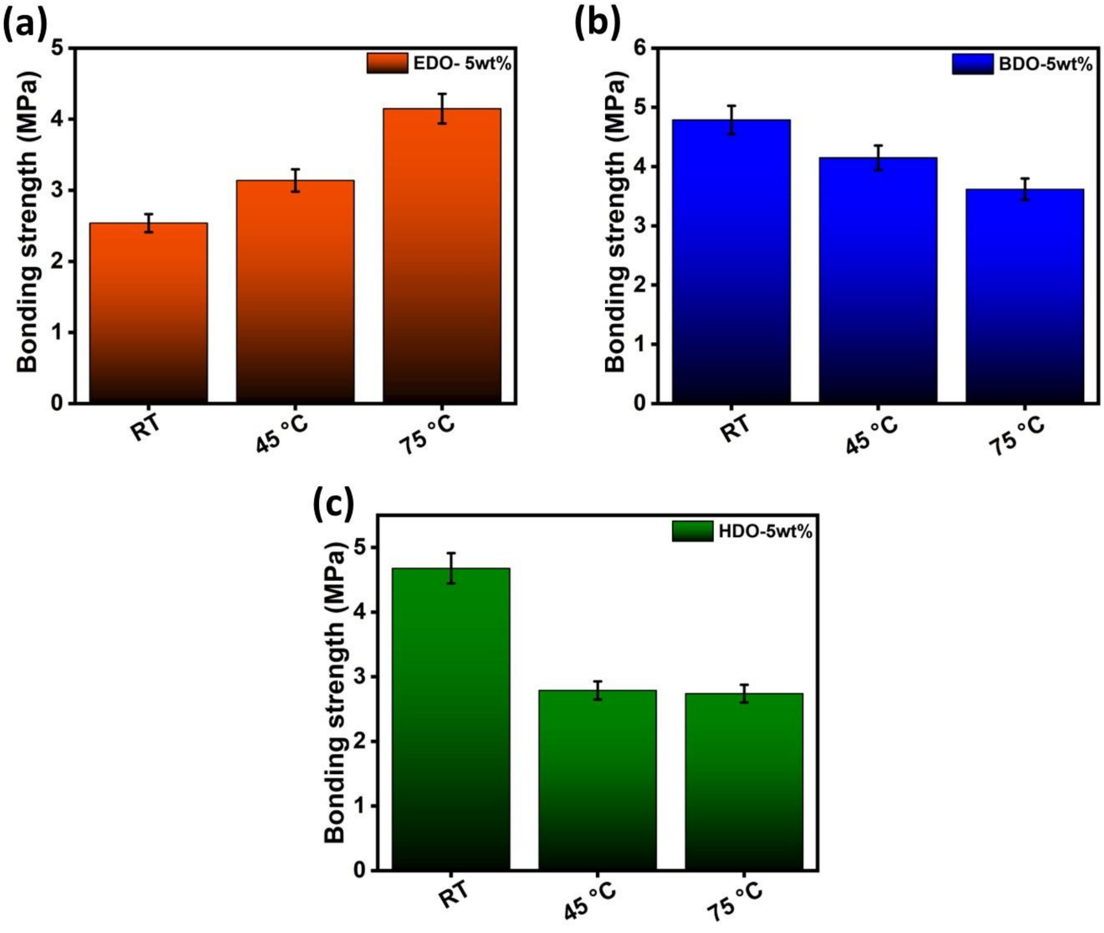

Figure 20: Bonding strength of (a) different temperatures of EDO in PU adhesive (b) different temperatures of BDO in PU adhesive (c) different temperatures of HDO in PU adhesive on oak wood.

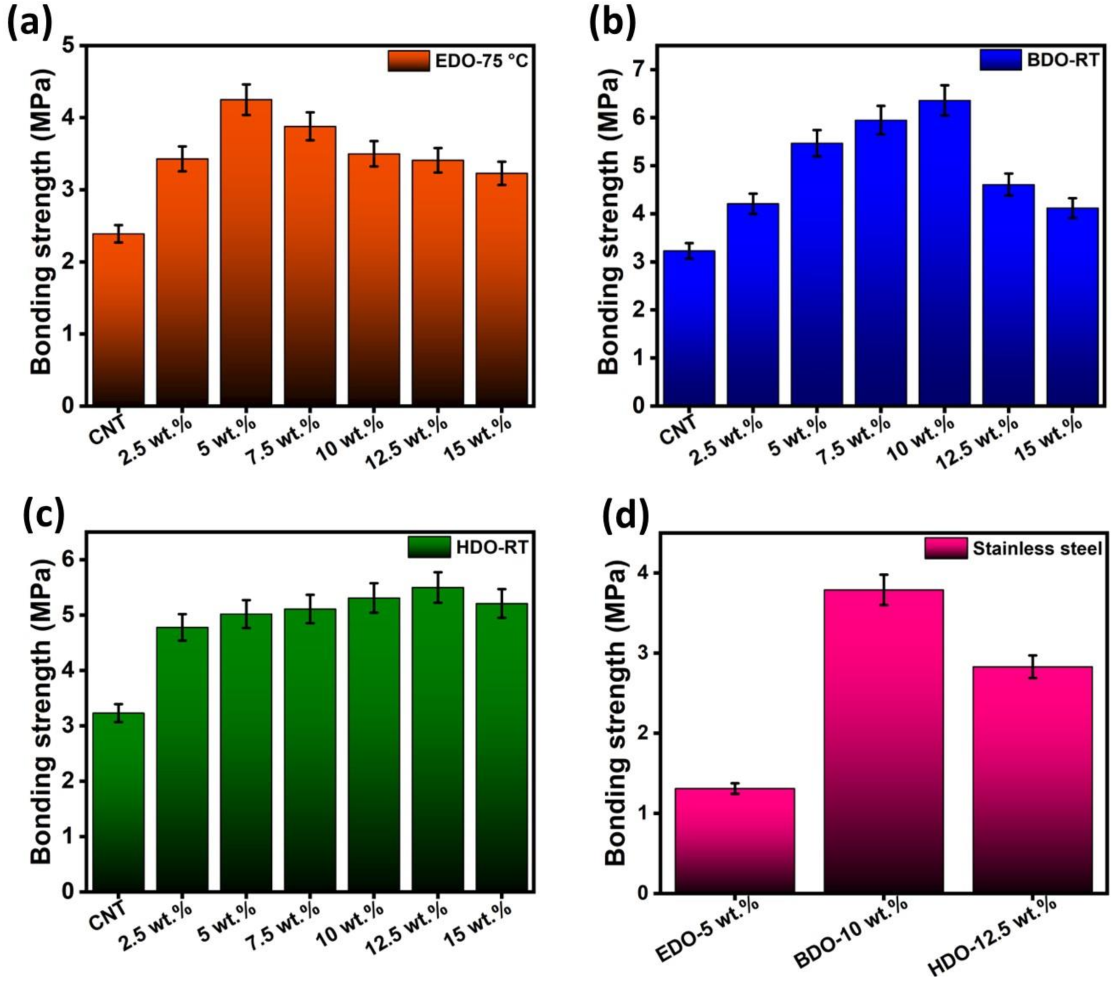

Figure 21: Bonding strength of (a) different wt.% of EDO in PU adhesive (b) different wt.% of BDO in PU adhesive (c) different wt.% of HDO in PU adhesive on oak wood (d) best sample bonding strength in PU adhesive on stainless-steel coupon.

3.3.2 Bonding strength on maple wood

After testing all samples for oak wood, the same crosslinker and the same temperature for curing the PU adhesive were tested on maple wood to study the bonding strength on another wood surface. **Figure 24** shows the bonding strength of adhesives on maple wood. The control sample at 75°C obtained 4.36 Mpa and at RT 4.47 Mpa. After adding EDO with varying wt.% bonding strength was inclined from 5.11 Mpa with 2.5 wt.% to 5.85 Mpa with 5 wt.%, this trend declined with higher wt.% and was observed at 4.56 Mpa (15 wt.%). After introducing BDO the bonding strength gradually increased and the higher bonding strength was observed at 6.76 Mpa with 10 wt.%, it declined incorporation of 12.5 wt.% and 15 wt.% from 5.69 Mpa to 5.33 Mpa. Moreover, the adhesive sample was crosslinked with HDO increasing trend was noted with good bonding strength. It increased from 6.28 Mpa (2.5 wt.%) to 7.79 Mpa (7.5 wt.%). For the 10 wt.% loaded sample slightly declined, bonding strength was recorded at 7.59 Mpa after this ratio 5.91 Mpa (12.5 wt.%) and 5.38 Mpa (15 wt.%) bonding strength was observed simultaneously. Here, all adhesive samples with each crosslinker show higher bonding strength than oak wood. This may be maple wood's physical properties, as wood contains cellulose, hemicellulose, and lignin, which can react with the chemical components of the adhesive sample and enhance the bonding strength. The lignin content was higher in maple wood than in oak wood. Along with that, maple wood has a diffuse pores structure while oak wood has ring pores. This factor could be responsible for the higher bonding strength of adhesives on maple wood.

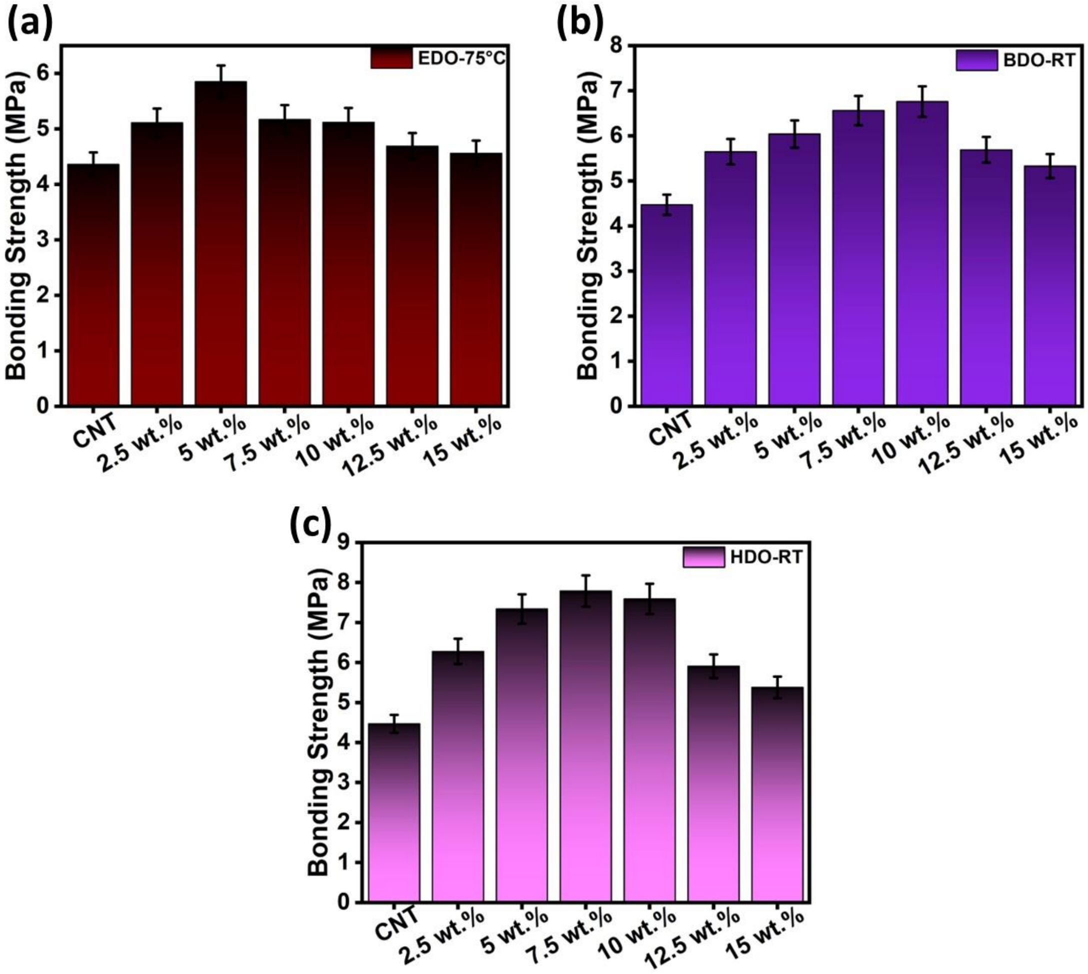

Figure 22: Bonding strength of (a) different wt.% of EDO in PU adhesive (b) different wt.% of BDO in PU adhesive (c) different wt.% of HDO in PU adhesive on maple wood.

3.4 Thermogravimetric analysis

TGA and its derivative thermograms (DTG) of control and adhesive samples with varying wt.% of three different diols are represented in **Figure 25 a, b** & **c**. The thermal decomposition behavior of adhesives, with varying chain extender concentrations, under the nitrogen atmosphere was studied. The initial degradation temperature shifts to a lower temperature with increasing the wt.% of diols in the polymeric sample which could be due to the stronger crosslinking network of the polymer as higher crosslinking is responsible for making a brittle polymer that cannot withstand higher temperatures. Moreover, the HDO-containing adhesive samples have shown increased thermal stability as compared with EDO and BDO-containing adhesive samples due to the longer aliphatic chain which contains many C-C bonds [83]. Moving forward to the DTG thermograms (**Figure 25 d, e & f**), all the adhesive samples and control samples have shown two-step thermal degradation in the temperature region from 200 ºC to 500 ºC. In the first stage, in the temperature range between 200 ℃ to 400 ℃, larger PU materials can be broken down into polyol and isocyanate, this process occurs in two stages: the first, from 200 ℃ to 350 ℃, involves the breakdown of smaller or unreacted molecules; the second, from 350 ℃ to 400 ℃, involves the dissociation of larger molecules. At a temperature above 400 ℃, the thermal degradation corresponds to the dissociation of the char layer formed in the previous phase [80]. Sample weight loss of 5% and 30% at decomposition temperatures ($T_{5\%}$ and $T_{30\%}$), maximum decomposition rate (T_{MAX}), heat resistance index temperature (T_{HRI}), glass transition temperature (T_g), and residual mass in wt.% are displayed in **Table 6**. T_{HRI} value is calculated using **equation 1** [84] [85]. The results show that the incorporation of chain extenders into all the samples leads to the increased thermal stability of all the samples compared to the control sample.

$$T_{HRI} = 0.49[T_{-5\%} + 0.6(T_{-30\%} - T_{-5\%})] \qquad (1)$$

Table 6: Comparison data of $T_{5\%}$, $T_{30\%}$, T_{MAX}, T_{HRI}, T_g, and residual mass

Sample name	**wt.%**	**$T_{5\%}$**	**$T_{30\%}$**	**$T_{MAX(\%)}$**	**T_{HRI}**	**T_g (°C)**	**Residual Mass (%)**
EDO-(75^{o}C)	CNT	299	357	394	163	8.72	6.45
	2.5%	282	363	384	161	-5.49	5.63
	5%	254	333	452	147	-9.57	0.46
	7.5%	280	364	448	161	-11.80	9.23
	10%	273	353	454	157	-13.40	9.69
	12.5%	263	340	436	151	-13.76	13.70
	15%	256	341	439	150	-14.78	12.08
BDO-(RT)	CNT	295	370	387	166	16.09	13.34
	2.5%	289	361	384	164	25	11.96
	5%	294	365	464	164	26.45	13.03
	7.5%	294	367	458	165	29.01	10.98
	10%	291	357	454	161	38.94	9.23
	12.5%	265	334	444	150	57.66	12.45
	15%	278	338	437	153	63.47	16.61
HDO-(RT)	CNT	295	370	387	166	16.09	13.34
	2.5%	290	368	386	165	21.18	7.75
	5%	290	369	447	165	22.55	8.99
	7.5%	291	364	448	164	26.47	8.60
	10%	288	366	456	164	40.80	10.40
	12.5%	298	359	454	163	49.91	8.99
	15%	284	341	437	155	57.80	14.49

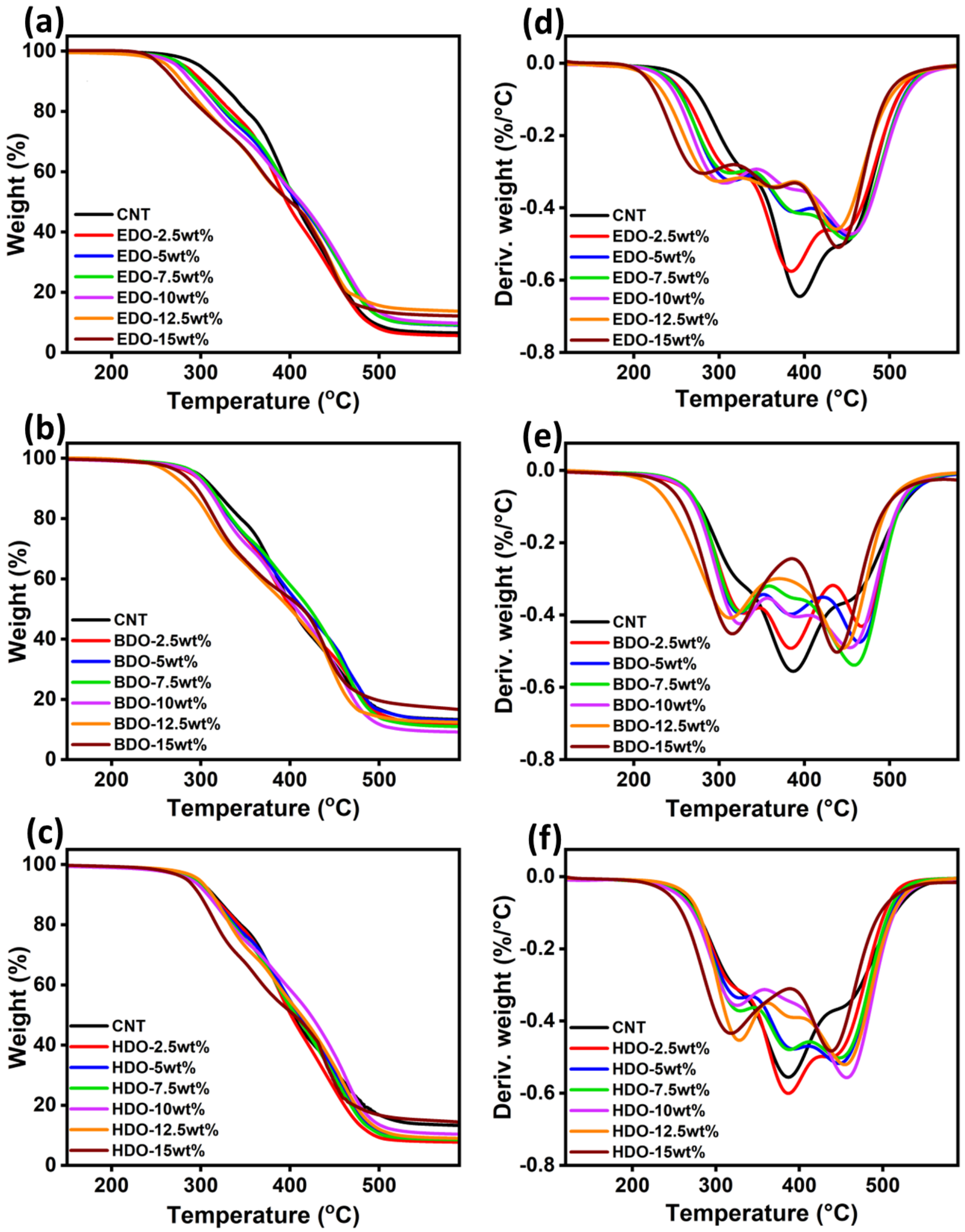

Figure 23: Thermogravimetric analysis (a) EDO- adhesive, (b) BDO- adhesive, (c) HDO-adhesive and derivative thermogram of (d) EDO- adhesive, BDO- adhesive and (f) HDO-adhesive samples with varying wt.% of diol.

3.5 Different scanning calorimetry

DSC graphs indicate the thermal transition temperature of all the adhesive samples having three different crosslinkers (EDO, BDO, and HDO) (**Figure 26**). The temperature range for all the experiments was from -50 ^{o}C to 300 ^{o}C, with a ramp rate of 10^{o}C/minute. For all the samples, with increasing wt.% of diols, the glass transition temperature is expected to be increased, but in the case of EDO adhesive samples the T_g is following the decreasing trend from 8.72 ^{o}C to -14.78 ^{o}C which could be due to a plasticizing effect of EDO, and, with increasing wt.% of EDO could be responsible for the pronounced plasticizing effect thus, leading to decreasing T_g. In contrast, the BDO and HDO-containing adhesive samples show an increasing trend from 16.09 ^{o}C to 63.47 ^{o}C and 16.09 ^{o}C to 57.80 ^{o}C, respectively, which could be due to the longer polymeric chain that could be more entangled. Hence, responsible for the increasing T_g [83]. In addition, as the chain extender rises, more cross-links form between polymer chains. The increased cross-linking may restrict the molecular mobility of the polymer, leading to a higher T_g value.

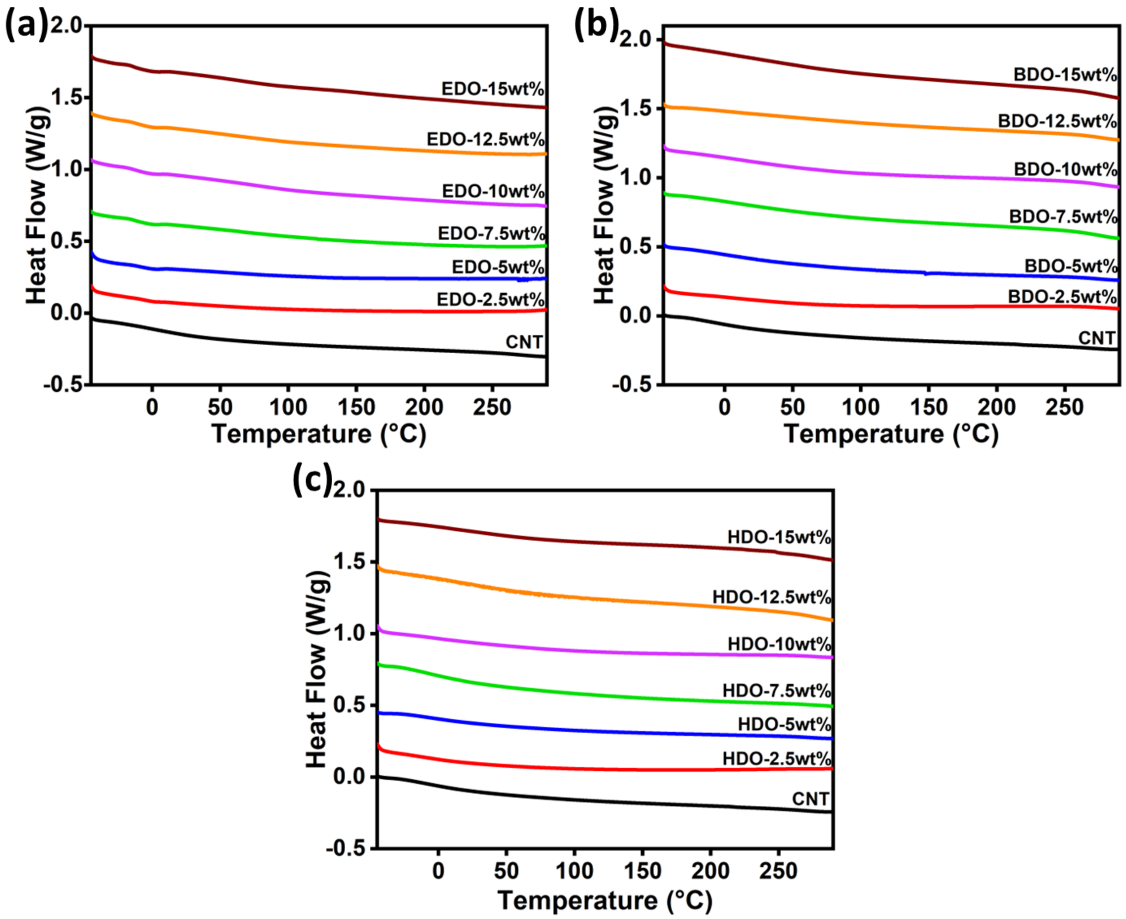

Figure 24: DSC of (a) EDO- PU adhesive with varying wt.% (b) BDO-PU adhesive with varying wt.% (c) HDO-PU adhesive with varying wt.% of diol.

3.6 Gel content and degree of swelling

The degree of swelling provides some information regarding a polymer's capability to absorb and retain a solvent, whereas the gel content is the insoluble fraction of a cross-linked polymer. To perform the test, the best adhesive sample (EDO-5 wt.%, BDO-10 wt.%, and HDO-12.5 wt.%) were immersed in two different solvents based on polar solvent (water) and non-polar solvent (toluene) for 24 h (**Figure 27**).

After that, the samples were dried in an oven at 70°C for 48 h (**Figure 27 b**). The swelling capability of the polymer is intrinsically related to its crosslinking degree and its interaction with a given solvent. In this sense, attractive interactions between a cross-linked polymer with solvent lead to a higher degree of swelling. The degree of swelling can be calculated through **Equation 2**.

$$DS\ (\%) = \frac{m_1 - m_0}{m_0} \times 100 \tag{2}$$

Where m_0 the initial is weight and m_1 is the weight after swelling. Fraction of the polymer itself is dissolved which is removed from the polymer structure upon drying. That condition leads to a reduction of the polymer’s weight in comparison to the initial weight of the polymer before swelling which allows the calculation of gel content through **Equation 3**. Where m_2 is the weight after drying.

$$GC\ (\%) = \frac{m_2}{m_0} \times 100 \tag{3}$$

Figure 27(a) represents the gel content of the best adhesive samples (based on bonding strength) from three different synthesized PU adhesives. At first glance, all the adhesive samples show almost 100% gel content in water which shows it is highly insoluble in water. It has a hydrophobic nature which can limit the penetration and swelling of the adhesive in aqueous environments. These higher results can correspond to a higher crosslinking network of polymeric adhesives. This increased crosslinking imparts greater bonding strength and rigidity to the material, making it more resistant to deformation. It may exhibit good thermal stability and resistance to heat. In addition, this makes them suitable for application were exposed to harsh chemicals or solvents. However, in toluene (non-polar solvent), the EDO-5 wt.% containing adhesive sample has shown around 75% gel content which is increased to 90% in the BDO-10 wt.% containing adhesive sample but decreased to 80% for the HDO-12.5 wt.% containing adhesive sample. Overall, BDO adhesive is more cross-linked than the other two adhesives. Thus, non-polar solvents affect higher to these synthesized adhesive materials than polar solvents.

Figure 27(b) shows the degree of swelling of the same materials. For polar solvent, DS is less than 10 % for all the materials which confirms that all materials are highly cross-linked. However, for non-polar solvent, the EDO-5 wt.% adhesive sample showed the lowest (35%) it is increased to almost 90% for the BDO-10 wt.% adhesive sample and it was decreased to 65% in HDO-12.5 wt.%. So, the polymer may have more affinity for non-polar solvents, it would swell more in toluene due to stronger interaction between non-polar parts of the polymer. In contrast, the polar nature of water may lead to weaker interactions with polymers, resulting in a lower swell percentage of these materials. Overall, these materials are highly cross-linked and have a higher hydrophobic nature. Along with this, after removing the samples from solvents and drying them in an oven at 70^{o}C for 48 h, the FT-IR spectra were carried out, and no major changes were observed (**Figure 28**).

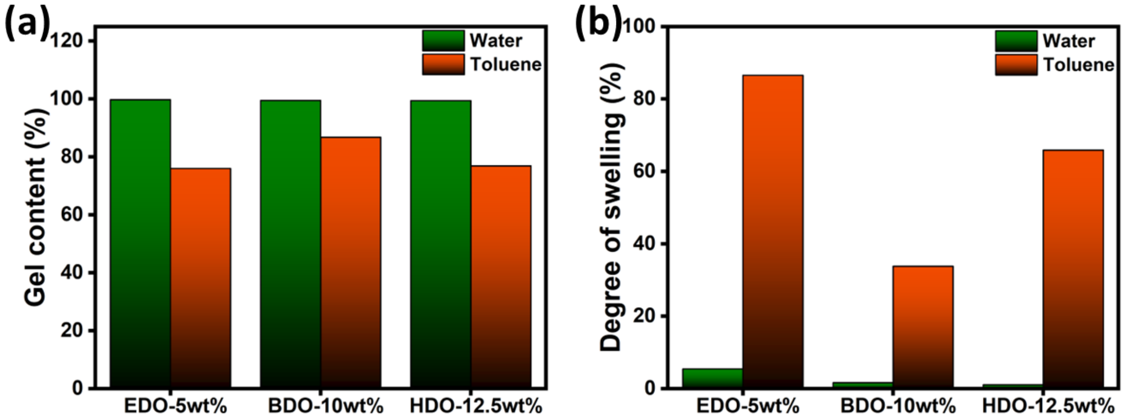

Figure 25: Percentage of gel content (a) and swelling degree (b) of EDO 5 wt.%, BDO-10 wt.% and HDO-12.5 wt.% in different solvents.

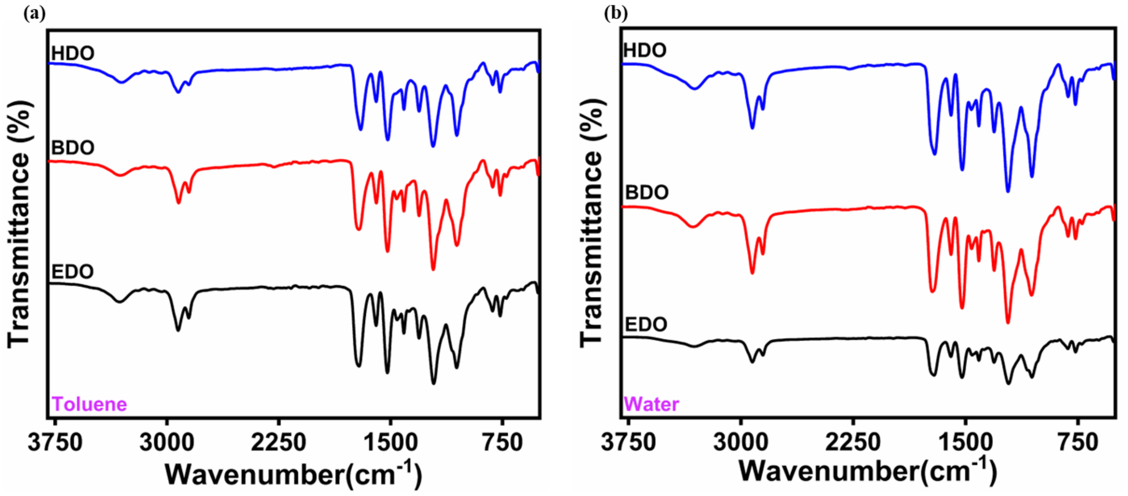

Figure 26: FT-IR spectra of a dried sample after performing gel and swelling test (a) toluene and (b) water.

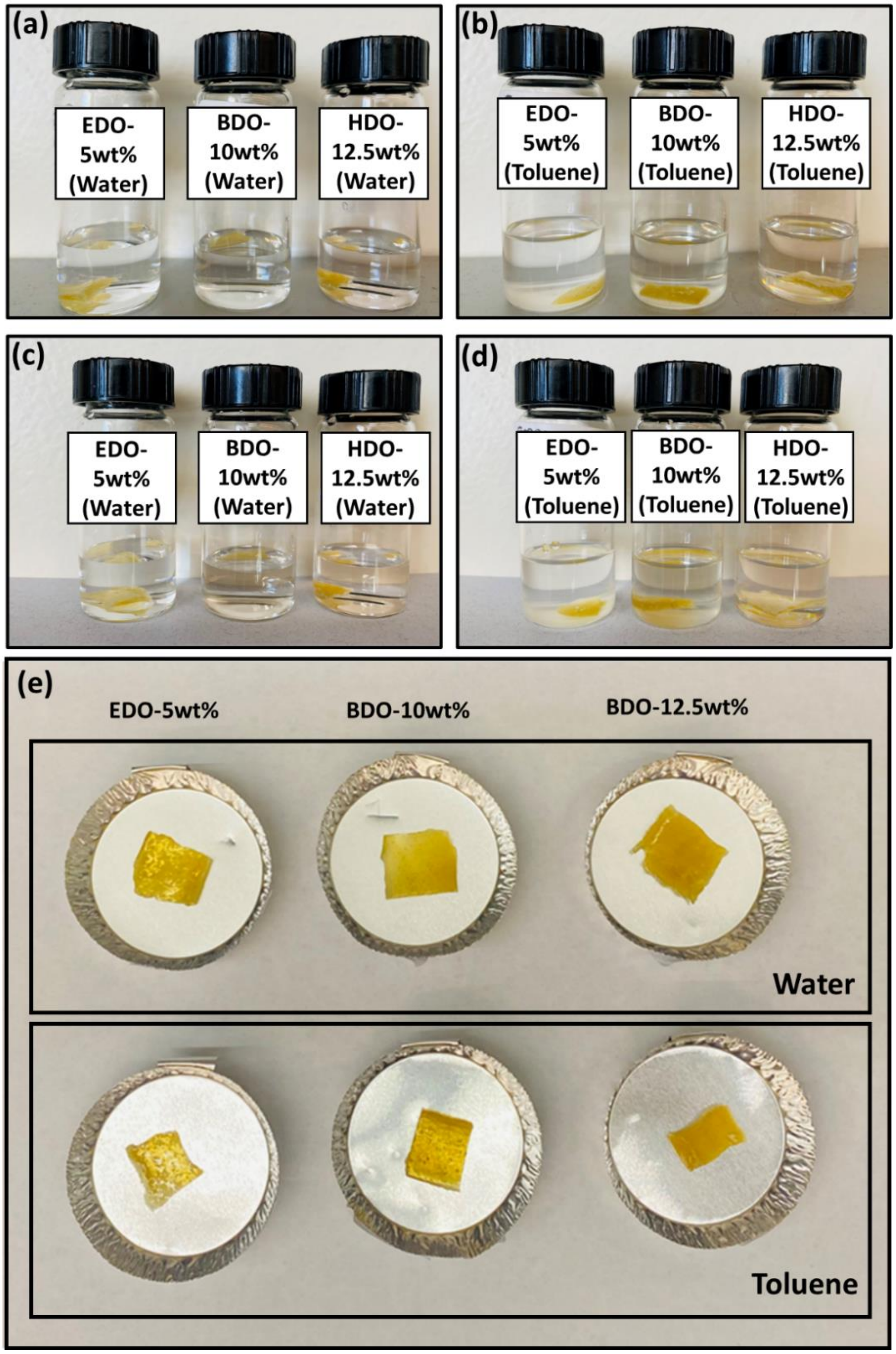

Figure 29: Picture of EDO-5 wt%, BDO-10 wt% and HDO-12.5 wt% (a,b) after putting into solvents (c,d) after 24 hours and I after drying in oven for 48 hours at 70°C.

3.7 Contact angle

The surface tension of a solid can be determined with the use of an Ossila Contact Angle Goniometer by measuring the angle formed between the solid and a droplet of liquid resting on the surface. When describing the relative affinity of water molecules to spreading on the surface of any substrate, the words hydrophilicity ($\theta < 90^o$) and hydrophobicity ($\theta > 90^o$) are used [86]. For measuring the contact angle, the best sample of adhesive (EDO-5 wt.%, BDO-10 wt.%, and HDO-12.5 wt.%) was applied to the glass surface and placed at room temperature for 24 hours. After the sample was cured, the contact angles for EDO, BDO, and HDO samples were performed with three different solvents: water, glycerol, and ethylene glycol (EG). **Figure 29** shows the contact angle measurement. In the case of water (**Figure 29 a, d & g**) the average contact angles for EDO, BDO, and HDO samples were noted at 91.21^o, 105.47^o, and 98.01^o, respectively. It was observed that the adhesive materials presented with above 90^o. This indicates the hydrophobic nature of the prepared adhesive. This means these properties can be applied where water resistance is necessary, such as in outdoor environments or in products that may encounter moisture. Upon decreasing the polarity of the solvents in the order of glycerol (**Figure 29 c, f & i)** and EG (**Figure 29b, e & h)** there was an overall decrease in the contact angle. With the use of EG, EDO-based adhesive was observed at 72.41^o, BDO was at 60.31^o and HDO was at 58.23^o. In addition, with the glycerol solvent results were noted above 80^o in EDO and BDO, while the contact angle measurement with HDO was at 75.76^o simultaneously, which reinforced the hydrophobic behavior of the adhesive samples.

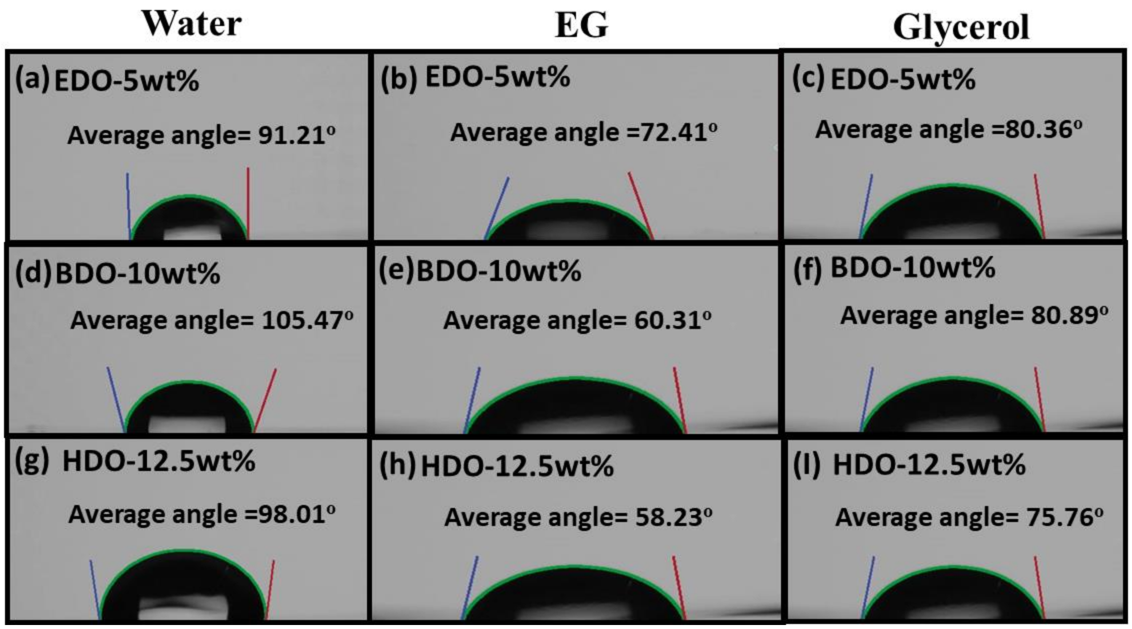

Figure 30: Contact angle of (a-c) EDO-5 wt.%, (d-f) BDO-10 wt.%, and (g-i) HDO-12.5wt.% adhesive samples with water, EG, and glycerol.

CHAPTER IV

CONCLUSION

In this research, bio-based wood adhesives were prepared using soybean oil polyol which represents an alternative to petroleum-based adhesives. Soybean oil polyol was synthesized through the epoxidation reaction followed by a ring-opening reaction. To confirm the formation of polyol, characteristic tests such as FT-IR, GPC, and wet chemistry were also performed. To enhance the bonding strength of PU adhesive three chain extenders were introduced, which showed better results with higher bonding strength. After increasing the weight percentage of the chain extender, the bonding strength was increased from 3 MPa to 6.36 MPa on oak wood after incorporating 10 wt.% of BDO. This is due to the additional cross-linking of the chain extender. After getting good strength on oak wood, the other two substrates were introduced to check the bonding strength on various specimens like maple wood and stainless-steel coupons. Moreover, on maple wood, bonding strength was inclined from 4.47 MPa to 6.76 MPa (BDO-10 wt.%), and 7.79 MPa (HDO-7.5 wt.%). While on metal coupons the best result was observed at 3.39 MPa with the best adhesive sample of (BDO-10 wt.%). Meanwhile, the trend in DSC graphs revealed a correlation between the incorporation of crosslinkers and the glass transition temperature in adhesive samples. Higher concentrations of BDO and HDO crosslinkers led to increased T_g temperatures, indicating enhanced cross-linking and reduced polymer mobility. This indicates a direct influence of cross-linker concentration on the thermal transition behavior of the formed adhesive. Three materials display excellent stability in water and toluene. BDO adhesive’s lower swelling and higher gel content contribute to its superior bonding strength (6.36 MPa) compared to the other two PU adhesives. These results lead to the emphasis the cross-linking in analysing adhesive material properties. The adhesive samples incorporating EDO-5 wt.%, BDO-10 wt.%, and HDO-12.5 wt.% crosslinkers exhibited a hydrophobic nature, as indicated by contact angles exceedingly above 90^o in water. Hence, the hydrophobic nature of the adhesive materials makes them better to use in wet environments as well. Without any solvent or catalyst successfully formed PU adhesive. This work provides a sustainable alternative to petroleum-based adhesives with good bonding and physical properties.

CHAPTER V

FUTURE WORK

Moreover, there is potential for exploring the synthesis of a fully bio-based adhesive by circumventing the use of MDI. This approach would facilitate a comparative analysis of adhesion strength between MDI-based and bio-based adhesive formulations. By eliminating MDI, which is derived from petroleum, the feasibility of developing environmentally sustainable alternatives can be assessed. Furthermore, an intriguing avenue for research involves substituting diols with diamines and synthesizing them with carbonated polyol to produce non-isocyanate polyurethane (NIPU). This synthesis route not only avoids the use of isocyanates, which are associated with health and environmental concerns but also aligns with green chemistry principles. Investigating the bonding strength and other pertinent properties of NIPU-based adhesives would contribute to advancing eco-friendly adhesive technologies. In summary, exploring the substitution of diols, the synthesis of bio-based adhesives sans MDI, and the development of NIPU-based formulations represents promising directions for future research endeavors in adhesive chemistry. These investigations hold the potential for enhancing adhesive performance while mitigating environmental impact, thus fostering sustainable solutions in materials science and engineering.

REFERENCES

[1] U. Panchal, M.L. Chaudhary, P. Patel, J. Patel, R.K. Gupta, Soybean-Based Bio-Adhesives: Role of Diamine on the Adhesive Properties, ACS Omega. 9 (2024) 10738–10747.

[2] P. Patel, R. Patel, J. Chaudhari, R.K. Gupta, Role of crosslinkers on the properties of bio-based wood adhesives, Polym. Eng. Sci. (2024) Just Accepted (10.1002/pen.26729).

[3] A. Tenorio-Alfonso, M.C. Sánchez, J.M. Franco, A Review of the Sustainable Approaches in the Production of Bio-based Polyurethanes and Their Applications in the Adhesive Field, J. Polym. Environ. (2020) 1–26.

[4] A. Sionkowska, Current research on the blends of natural and synthetic polymers as new biomaterials: Review, Prog. Polym. Sci. 36 (2011) 1254–1276.

[5] F.M. de Souza, M.R. Sulaiman, R.K. Gupta, Materials and Chemistry of Polyurethanes, in: Mater. Chem. Flame-Retardant Polyurethanes Vol. 1 A Fundam. Approach, American Chemical Society, 2021: p. 1.

[6] J. Peyrton, L. Avérous, Structure-properties relationships of cellular materials from biobased polyurethane foams, Mater. Sci. Eng. R Reports. 145 (2021) 100608.

[7] H.M.C.C. Somarathna, S.N. Raman, D. Mohotti, A.A. Mutalib, K.H. Badri, The use of polyurethane for structural and infrastructural engineering applications: A state-of-the-art review, Constr. Build. Mater. 190 (2018) 995–1014.

[8] C. Liang, U.R. Gracida-Alvarez, E.T. Gallant, P.A. Gillis, Y.A. Marques, G.P. Abramo, T.R. Hawkins, J.B. Dunn, Material Flows of Polyurethane in the United States, Environ. Sci. Technol. 55 (2021) 14215–14224.

[9] J. Guan, Y. Song, Y. Lin, X. Yin, M. Zuo, Y. Zhao, X. Tao, Q. Zheng, Progress in Study of Non-Isocyanate Polyurethane Progress in Study of Non-Isocyanate Polyurethane, Ind. Eng. Chem. 50 (2017) 6517–6527.

[10] E. Sharmin, F. Zafar, Chapter 1 :Polyurethane: An Introduction, Polyurethane. (2012) 1–14.

[11] H. Sardon, D. Mecerreyes, A. Basterretxea, L. Avérous, C. Jehanno, From Lab to Market: Current Strategies for the Production of Biobased Polyols, ACS Sustain. Chem. Eng. 9 (2021) 10664–10677.

[12] P. Sahu, L. Sharma, T. Dawsey, R.K. Gupta, Insight into the synthesis and thermomechanical properties of “short-long” type biobased aliphatic polyesters, J. Appl. Polym. Sci. 141 (2024) e54972.

[13] J.O. Akindoyo, M.D.H. Beg, S. Ghazali, M.R. Islam, N. Jeyaratnam, A.R. Yuvaraj, Polyurethane types, synthesis and applications-a review, RSC Adv. 6 (2016) 114453–114482.

[14] G. Tersac, Chemistry and technology of polyols for polyurethanes. Milhail Ionescu. Rapra Technology, Shrewsbury, UK, Polym. Int. 56 (2007) 820–820.

[15] R.K. Gupta, M. Ionescu, X. Wan, D. Radojcic, N. Bilic, New polyols with isocyanuric structure by thiol-ene “click” chemistry reactions, J. Cell. Plast. 53 (2017) 639–662.

[16] F. M. de Souza, J. Choi, S. Bhoyate, P.K. Kahol, R.K. Gupta, Expendable Graphite as an Efficient Flame-Retardant for Novel Partial Bio-Based Rigid Polyurethane Foams, C — J. Carbon Res. 6 (2020) 27.

[17] C. Zhang, S. Bhoyate, M. Ionescu, P.K. Kahol, R.K. Gupta, Highly flame retardant

and bio-based rigid polyurethane foams derived from orange peel oil, Polym. Eng. Sci. 58 (2018) 2078–2087.

[18] F.M. de Souza, R.K. Gupta, Waterborne Polyurethanes in Sustainability Development, in: Sustain. Prod. Appl. Waterborne Polyurethanes, Springer, Cham, 2021: pp. 83–108.

[19] R.K. Gupta, A.K. Mishra, Eco-friendly Waterborne Polyurethanes: Synthesis, Properties, and Applications, CRC Press, Boca Raton, FL, 2022.

[20] A.S. More, T. Lebarbé, L. Maisonneuve, B. Gadenne, C. Alfos, H. Cramail, Novel fatty acid based di-isocyanates towards the synthesis of thermoplastic polyurethanes, Eur. Polym. J. 49 (2013) 823–833.

[21] O. Jaudouin, J.J. Robin, J.M. Lopez-Cuesta, D. Perrin, C. Imbert, Ionomer-based polyurethanes: A comparative study of properties and applications, Polym. Int. 61 (2012) 495–510.

[22] T.A.P. Hai, M. Tessman, N. Neelakantan, A.A. Samoylov, Y. Ito, B.S. Rajput, N. Pourahmady, M.D. Burkart, Renewable polyurethanes from sustainable biological precursors, Biomacromolecules. 22 (2021) 1770–1794.

[23] N. V Gama, A. Ferreira, A. Barros-Timmons, Polyurethane foams: Past, present, and future, Materials (Basel). 11 (2018) 1841.

[24] K. Skleničková, S. Abbrent, M. Halecký, V. Kočí, H. Beneš, Biodegradability and ecotoxicity of polyurethane foams: A review, Crit. Rev. Environ. Sci. Technol. 52 (2022) 157–202.

[25] V. Kanyanta, A. Ivankovic, Mechanical characterisation of polyurethane elastomer for biomedical applications, J. Mech. Behav. Biomed. Mater. 3 (2010) 51–62.

[26] A.K. Bledzki, S. Reihmane, J. Gassan, Thermoplastics reinforced with wood fillers: a literature review, Polym. - Plast. Technol. Eng. 37 (1998) 451–468.

[27] B.B.R. Silva, R.M.C. Santana, M.M.C. Forte, A solventless castor oil-based PU adhesive for wood and foam substrates, Int. J. Adhes. Adhes. 30 (2010) 559–565.

[28] A.H. Bezerra, S.R. Bezerra, N.S. Macêdo, Z. de Sousa Silveira, C.R. dos Santos Barbosa, T.S. de Freitas, D.F. Muniz, D.L. de Sousa Júnior, J.P.S. Júnior, I.A. Donato, H.D.M. Coutinho, F.A.B. da Cunha, Effect of estragole over the RN4220 Staphylococcus aureus strain and its toxicity in Drosophila melanogaster, Life Sci. 264 (2021).

[29] S. Nishimura, Book re v iews Book re v iews, New York. 8 (2001) 293–300.

[30] C.S. Schollenberger, Polyurethane Elastomers BT - Rubber Technology, in: M. Morton (Ed.), Springer Netherlands, Dordrecht, 1999: pp. 438–464.

[31] N. Polyurethane, E. Delebecq, J. Pascault, B. Boutevin, U. De Lyon, On the Versatility of Urethane / Urea Bonds : Reversibility , Blocked, (2013).

[32] K.S. Wenk, A. Ehrlich, Isocyanates, Dermatitis. 23 (2012) 130–131.

[33] S. Ebnesajjad, Characteristics of Adhesive Materials, Elsevier Inc., 2010.

[34] I. Skeist, J. Miron, History of Adhesives, J. Macromol. Sci. Part A - Chem. 15 (1981) 1151–1163.

[35] B. Na, A. Pizzi, L. Delmotte, X. Lu, One-component polyurethane adhesives for green wood gluing: Structure and temperature-dependent creep, J. Appl. Polym. Sci. 96 (2005) 1231–1243.

[36] M. Schubert, O. Kläusler, Applying machine learning to predict the tensile shear strength of bonded beech wood as a function of the composition of polyurethane

prepolymers and various pretreatments, Wood Sci. Technol. 54 (2020) 19–29.

[37] K.H. Badri, A.H. Ujar, Z. Othman, F.H. Sahaldin, Shear strength of wood to wood adhesive based on palm kernel oil, J. Appl. Polym. Sci. 100 (2006) 1759–1764.

[38] S.D. Desai, J. V. Patel, V.K. Sinha, Polyurethane adhesive system from biomaterial-based polyol for bonding wood, Int. J. Adhes. Adhes. 23 (2003) 393–399.

[39] K.P. Somani, S.S. Kansara, N.K. Patel, A.K. Rakshit, Castor oil based polyurethane adhesives for wood-to-wood bonding, Int. J. Adhes. Adhes. 23 (2003) 269–275.

[40] A. Ortiz-Fernández, F.A. Carrillo-Sánchez, L.H. May-Hernández, R.J. Estrada-León, H.J. Carrillo-Escalante, F. Hernández-Sánchez, A. Valadez-Gonzalez, Design of experiments for optimization a biodegrable adhesive based on ramon starch (Brosimum alicastrum Sw.), Int. J. Adhes. Adhes. 73 (2017) 28–37.

[41] X. Kong, G. Liu, J.M. Curtis, Characterization of canola oil based polyurethane wood adhesives, Int. J. Adhes. Adhes. 31 (2011) 559–564.

[42] A. Technology, Handbook of Adhesion Technology, Handb. Adhes. Technol. (2011).

[43] F. Awaja, M. Gilbert, G. Kelly, B. Fox, P.J. Pigram, Adhesion of polymers, Prog. Polym. Sci. 34 (2009) 948–968.

[44] L. Gollob, J.D. Wellons, Wood Adhesion, Handb. Adhes. (1990) 598–610.

[45] S.J. Marshall, S.C. Bayne, R. Baier, A.P. Tomsia, G.W. Marshall, A review of adhesion science., Dent. Mater. 26 (2010) e11-6.

[46] M. Kłonica, Analysis of the effect of selected factors on the strength of adhesive

joints, IOP Conf. Ser. Mater. Sci. Eng. 393 (2018).

[47] R.M. Rowell, R. Pettersen, M.A. Tshabalala, Cell wall chemistry, Handb. Wood Chem. Wood Compos. Second Ed. (2012) 33–72.

[48] S.R. Chandrasekaran, P.K. Hopke, L. Rector, G. Allen, L. Lin, Chemical composition of wood chips and wood pellets, Energy and Fuels. 26 (2012) 4932–4937.

[49] A. Le Floch, M. Jourdes, P.L. Teissedre, Polysaccharides and lignin from oak wood used in cooperage: Composition, interest, assays: A review, Carbohydr. Res. 417 (2015) 94–102.

[50] S. Magalhães, L. Alves, B. Medronho, A.C. Fonseca, A. Romano, J.F.J. Coelho, M. Norgren, Brief overview on bio-based adhesives and sealants, Polymers (Basel). 11 (2019).

[51] M. Jawaid, T. Khan, M. Nasir, M. Asim, Eco-Friendly Adhesives for Wood and Natural Fiber Composites, 2021.

[52] F. Ferdosian, Z. Pan, G. Gao, B. Zhao, Bio-based adhesives and evaluation for wood composites application, Polymers (Basel). 9 (2017) 70.

[53] C.W. Paul, Hot-melt adhesives, MRS Bull. 28 (2003) 440–444.

[54] L.A. Heinrich, Future opportunities for bio-based adhesives-advantages beyond renewability, Green Chem. 21 (2019) 1866–1888.

[55] M.H. Hussin, N.H. Abd Latif, T.S. Hamidon, N.N. Idris, R. Hashim, J.N. Appaturi, N. Brosse, I. Ziegler-Devin, L. Chrusiel, W. Fatriasari, F.A. Syamani, A.H. Iswanto, L.S. Hua, S.S.A.O. Al Edrus, W.C. Lum, P. Antov, V. Savov, M.A. Rahandi Lubis, L. Kristak, R. Reh, J. Sedliačik, Latest advancements in high-

performance bio-based wood adhesives: A critical review, J. Mater. Res. Technol. 21 (2022) 3909–3946.

[56] A.M. Borrero-López, D.B. Guzmán, J.A. González-Delgado, J.F. Arteaga, C. Valencia, U. Pischel, J.M. Franco, Toward UV-Triggered Curing of Solvent-Free Polyurethane Adhesives Based on Castor Oil, ACS Sustain. Chem. Eng. 9 (2021) 11032–11040.

[57] C.C. Addis, R.S. Koh, M.B. Gordon, Preparation and characterization of a bio-based polymeric wood adhesive derived from linseed oil, Int. J. Adhes. Adhes. 102 (2020) 102655.

[58] D. Wei, J. Zeng, Q. Yong, High-Performance Bio-Based Polyurethane Antismudge Coatings Using Castor Oil-Based Hyperbranched Polyol as Superior Cross-Linkers, ACS Appl. Polym. Mater. 3 (2021) 3612–3622.

[59] M.A. Sawpan, Polyurethanes from vegetable oils and applications: a review, J. Polym. Res. 25 (2018).

[60] D. Vnučec, A. Kutnar, A. Goršek, Soy-based adhesives for wood-bonding–a review, J. Adhes. Sci. Technol. 31 (2017) 910–931.

[61] E. Orgilés-Calpena, F. Arán-Aís, A.M. Torró-Palau, C. Orgilés-Barceló, Synthesis and characterisation of potentially biodegradable polyurethane adhesives from soybased polyols, Polym. from Renew. Resour. 5 (2014) 99–114.

[62] K. Hill, Fats and Oils as Oleochemical Raw Materials, J. Oleo Sci. 50 (2001) 433–444.

[63] L.R. Barros Dourado, L.A. Fonseca Pascoal, N. Kazue, F.G. Perazzo Costa, D. Biagiotti, Soybeans (Glycine max) and Soybean Products in Poultry and Swine

Nutrition, Recent Trends Enhancing Divers. Qual. Soybean Prod. (2011).

[64] Y.-L. Cheng, C.-Y. Lee, Y.-L. Huang, C.A. Buckner, R.M. Lafrenie, J.A. Dénommée, J.M. Caswell, D.A. Want, G.G. Gan, Y.C. Leong, P.C. Bee, E. Chin, A.K.H. Teh, S. Picco, L. Villegas, F. Tonelli, M. Merlo, J. Rigau, D. Diaz, M. Masuelli, S. Korrapati, P. Kurra, S. Puttugunta, S. Picco, L. Villegas, F. Tonelli, M. Merlo, J. Rigau, D. Diaz, M. Masuelli, M. Tascilar, F.A. de Jong, J. Verweij, R.H.J. Mathijssen, We are IntechOpen , the world ' s leading publisher of Open Access books Built by scientists , for scientists TOP 1 %, Intech. 11 (2016) 13.

[65] T.E. Clemente, E.B. Cahoon, Soybean oil: Genetic approaches for modification of functionality and total content, Plant Physiol. 151 (2009) 1030–1040.

[66] P. Furtwengler, L. Avérous, Renewable polyols for advanced polyurethane foams from diverse biomass resources, Polym. Chem. 9 (2018) 4258–4287.

[67] A. Lopez, E. Degrandi, E. Canetta, J.L. Keddie, C. Creton, J.M. Asua, Simultaneous free radical and addition miniemulsion polymerization: Effect of the diol on the microstructure of polyurethane-acrylic pressure-sensitive adhesives, Polymer (Guildf). 52 (2011) 3021–3030.

[68] J. Li, J. Luo, X. Li, Z. Yi, Q. Gao, J. Li, Soybean meal-based wood adhesive enhanced by ethylene glycol diglycidyl ether and diethylenetriamine, Ind. Crops Prod. 74 (2015) 613–618.

[69] P.S. Zade, M.B. Mandake, S. Walke, N. Mumbai, Ijtrd16303, 5 (2018).

[70] Neswati, N. Nazir, Combination of temperature and time in epoxidation for producing epoxidized palm oil as source of bio polyol, IOP Conf. Ser. Earth Environ. Sci. 757 (2021).

[71] M. Fallah-Mehrjardi, A.R. Kiasat, K. Niknam, Nucleophilic ring-opening of epoxides: trends in β-substituted alcohols synthesis, Springer Berlin Heidelberg, 2018.

[72] J. Zhang, J.J. Tang, J.X. Zhang, Polyols prepared from ring-opening epoxidized soybean oil by a castor oil-based fatty diol, Int. J. Polym. Sci. 2015 (2015).

[73] M.A. Asare, P. Kote, S. Chaudhary, F.M. de Souza, R.K. Gupta, Sunflower Oil as a Renewable Resource for Polyurethane Foams: Effects of Flame-Retardants, Polymers (Basel). 14 (2022) 5282.

[74] Z. Jankauskiene, B. Butkute, E. Gruzdeviene, J. Cesevičiene, A.L. Fernando, Chemical composition and physical properties of dew- and water-retted hemp fibers, Ind. Crops Prod. 75 (2015) 206–211.

[75] S. Jiang, S. Zha, L. Xia, R. Guan, Synthesis and characterization of diphenylsilanediol modified epoxy resin and curing agent, J. Adhes. Sci. Technol. 29 (2015) 641–656.

[76] Y. Guo, R.M. Bustin, Micro-FTIR spectroscopy of liptinite macerals in coal, Int. J. Coal Geol. 36 (1998) 259–275.

[77] M. Iqhrammullah, Marlina, R. Hedwig, I. Karnadi, K.H. Kurniawan, N.G. Olaiya, M.K. Mohamad Haafiz, H.P.S. Abdul Khalil, S.N. Abdulmadjid, Filler-modified castor oil-based polyurethane foam for the removal of aqueous heavy metals detected using laser-induced breakdown spectroscopy (LIBS) technique, Polymers (Basel). 12 (2020).

[78] L.D. Antonino, I. Sumerskii, A. Potthast, T. Rosenau, M.I. Felisberti, D.J. dos Santos, Lignin-Based Polyurethanes from the Blocked Isocyanate Approach:

Synthesis and Characterization, ACS Omega. 8 (2023) 27621–27633.

[79] A. Al-Sharafi, B.S. Yilbas, H. Ali, H. Al-Qahtani, Adhesion of a water droplet on inclined hydrophilic surface and internal fluidity, Int. J. Adhes. Adhes. 96 (2020) 102464.

[80] A. Tenorio-Alfonso, M.C. Sánchez, J.M. Franco, Preparation, characterization and mechanical properties of bio-based polyurethane adhesives from isocyanate-functionalized cellulose acetate and castor oil for bonding wood, Polymers (Basel). 9 (2017) 1–14.

[81] N.M. Ito, J.R. Gouveia, S.E. Vidotti, M.J.G.C. Ferreira, D.J. dos Santos, Interplay of polyurethane mechanical properties and practical adhesion of flexible multi-layer laminates, J. Adhes. 96 (2020) 1219–1232.

[82] J. Peng, F. Liu, F. Feng, X. Feng, J. Cui, Enhancing Environmentally Friendly Tannin Adhesive for Plywood through Hyperbranched Polyamide, ACS Sustain. Chem. Eng. 11 (2023) 13805–13811.

[83] P. Patel, F.M. De Souza, R.K. Gupta, Study of Soybean Oil-Based Non-Isocyanate Polyurethane Films via a Solvent and Catalyst-Free Approach, (2024).

[84] H. Niu, H. Nabipour, X. Wang, L. Song, Y. Hu, Phosphorus-Free Vanillin-Derived Intrinsically Flame-Retardant Epoxy Thermoset with Extremely Low Heat Release Rate and Smoke Emission, ACS Sustain. Chem. Eng. 9 (2021) 5268–5277.

[85] M.M. Aung, Z. Yaakob, S. Kamarudin, L.C. Abdullah, Synthesis and characterization of Jatropha (Jatropha curcas L.) oil-based polyurethane wood adhesive, Ind. Crops Prod. 60 (2014) 177–185.

[86] R.S. Hebbar, A.M. Isloor, A.F. Ismail, Contact Angle Measurements, Elsevier

B.V., 2017.